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**HANDBOOK OF
CHEMICAL MICROSCOPY**

VOLUME I

Principles and Use of Microscopes and Accessories
Physical Methods for the Study of Chemical Problems

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HANDBOOK OF CHEMICAL MICROSCOPY

BY

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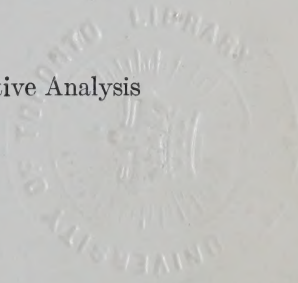
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VOLUME II

Chemical Methods and Inorganic Qualitative Analysis



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PREFACE

In spite of the continual growth which microscopical qualitative analysis has undergone, it is noteworthy that the methods of this branch of chemistry, as taught by Behrens in the early nineties, stand with little need for modification. Additional tests have been devised, new reactions and manipulative procedures have been utilized, but few of those which he first proposed have failed to stand the test of the last forty years. Building better than he knew, he chose reagents which are still unexcelled for convenience, rapidity, and versatility.

The development of microscopical qualitative analysis has been largely in the direction of new specific tests and identity reactions for relatively pure materials, rather than of new group reagents. Modifications of technique and of apparatus have been numerous, and the applications of microscopical tests have extended to the most diverse fields of chemistry and its related sciences.

Some of these applications are of long standing, though the methods have been improved and amplified in the course of years. The identification of mineral grains in ores and rocks; of the inorganic constituents in plant tissues, foods, and vegetable drugs; and of the various raw materials and products of chemical and other industries, are fields in which the uses of microscopical qualitative analysis have shown particular expansion, and in which many new procedures have originated. Although the present volume is limited to inorganic analysis, the manipulative technique and general principles will be found applicable to studies of organic reactions.

Any work on analytical chemistry, unless it ignores all previously existing and tested procedures, must be in large part a compilation; the present one is no exception. The authors acknowledge first of all their indebtedness to Behrens' fundamental contributions. They have made little attempt to cite in detail the original sources of reactions and tests which have long been the common property of chemists, and they make no claim to originality except in regard to a small proportion of the methods presented.

However, the choice of reagents and technique has not been without discrimination, and only methods which hold promise of general usefulness in microscopic analytical work have been included. All but the newest ones of these have been tested not only by the authors but also in the hands of students, and the various precautions indicated, though perhaps unnecessarily detailed, have been based on the difficulties likely to be encountered by workers having only an ordinary knowledge of inorganic and analytical chemistry.

The inclusive field of "microchemistry," which comprises all chemical procedures dealing with small amounts of material, is discussed only as regards those portions of it which involve microscopical qualitative reactions. Quantitative methods, volumetric and gravimetric, are therefore omitted; quantitative analyses of heterogeneous mixtures are discussed in Volume I.

Brief experiments are given to illustrate the behavior of the more common elements, and to constitute the basis for a course of instruction in microscopic qualitative analysis.

In response to repeated requests, photomicrographs of most of the common and useful tests have been included, not without some misgivings, for the authors believe that the mere examination of pictures will not take the place of the preparation and direct study of actual tests. The user of this book is urged to carry out the various experiments, and others which will suggest themselves, and to see for himself not only the commonly prevailing types of crystals which have been selected for the illustrations, but also the variations from these "normal" appearances. Only by so doing can he acquire the experience and judgment in interpretation, and the manipulative skill, which are essential to intelligent and rapid analyses. If he will accompany this study by reference to the standard works on inorganic and analytical chemistry, he will find the procedures instructive in their chemical significance as well as a profitable means of rapid and direct analysis.

Volume II, like Volume I, is based upon "Elementary Chemical Microscopy"; the pages therein devoted to qualitative analysis have been entirely rewritten, greatly expanded, and presented from a somewhat different angle.

In the preparation of the book which is now superseded by this Handbook the senior author was greatly indebted to his friends and teachers, Professor S. H. Gage of Cornell University, Professor

Th. H. Behrens of the Polytechnic School of Delft, and Doctor E. Macé of the University of Nancy — pioneers in the science and art of applied microscopy — and he would be ungrateful indeed did he not acknowledge how much of their precepts, opinions and methods are reflected in the present volume.

E. M. C.
C. W. M.

BAKER LABORATORY OF CHEMISTRY,
November, 1930.

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HANDBOOK OF CHEMICAL MICROSCOPY

INTRODUCTION

In Volume I of this Handbook the observations of physical and physico-chemical phenomena have been discussed in their relation to qualitative analysis, to the study of industrial materials, and to the solution of problems arising in research. It is there shown that such observations often may be sufficient to establish the identity or the composition of a substance in question without the necessity of having recourse to chemical reactions.

Frequently, however, qualitative chemical analyses are required. These, when made by microscopic methods, enable the analyst to obtain results in a minimum of time, upon a minimum of material, with the expenditure of little labor and at a wholly negligible cost, and all with no sacrifice of accuracy.

Because only small amounts of materials are employed, speed is assured. Obviously a fraction of a cubic centimeter can be evaporated, decanted, or filtered in less time than will be required to perform the same manipulations with 100 cc. or 10 cc. If the methods are speedy, results are to be obtained with corresponding rapidity.

But speed and ability to analyze very minute amounts of material are not the only advantages of "micro-analysis"; many of the "micro" tests for cations and for anions are far superior in their certainty and dependability to the macroscopic tests for the same elements or compounds.

Microscopic qualitative chemical analysis requires a special technique, which, however, is readily acquired.

It is the aim of Volume II of this Handbook to describe the essential manipulative methods in detail and to present a compilation of the most dependable tests for the inorganic cations and anions.

In the selection of the tests discussed, the authors have been guided more by the applicability of the tests to the analysis of complex mixtures and by the certainty of the results obtained than by sensitivity of reaction. Many of the statements regarding sensitivities, interferences, or applicability of tests will be found at variance with the published results of others, usually in the direction of less optimistic conclusions.

Numerous interesting "micro" reactions are omitted, either because they are suitable only as identity tests on substantially pure substances and are of little use in mixtures of various unknown materials, or because they require a more precise control of concentrations, acidity, temperature, etc., than is practicable in a single drop of unknown composition on a microscope slide. In other words, with few exceptions, reactions have been included only if they will yield results under almost any conditions and in almost any combinations.

Color reactions and spot tests¹ are not discussed except in a few instances, because they do not involve microscopical observations or technique.

The incompleteness of the present work may perhaps be excused on two counts:

A large proportion of published methods and tests (both "micro" and "macro") are not described with reference to their behavior when applied to mixtures, and it has not been possible as yet to study all the interferences which undoubtedly exist.

A limited number of reactions are available for certain metals and acids, and although there is great need of discovering new ones or adapting existing reactions to microscopical use, a vast amount of investigation remains to be done. Until these necessary investigations have been carried further, serious gaps will exist in microscopical analytical methods. These shortcomings are, however, hardly more serious than those of macroscopic qualitative analysis, in which the various systems work nicely on

¹ See especially the work of Feigl and his pupils:

Feigl and Stern: *Zeits. anal. Chem.* **60**, 1 (1921).

Feigl and Neuber: *ibid.* **62**, 369 (1923).

Feigl: *Mikrochemie* **1**, 4 (1923); **6**, 50 (1928); Emich: *Mikrochem. Praktikum* (1931), pp. 137-146; *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* (1931).

Heller: *ibid.* **1**, 213 (1929); **8**, 33 (1930).

Holzer: *ibid.* **8**, 217 (1930).

a selected list of the more common ions but are spoiled by intruders.

In selecting methods for microscopical analysis, ease of manipulation has been an important consideration, even at the expense of sensitivity or minuteness of sample. Tests requiring special apparatus or successive separations have largely been omitted, as contrary to the chief advantages of chemical microscopy: ease and directness.

As teachers of the science of chemistry the authors have felt called upon to lay stress upon the chemical properties of the different ions discussed, particularly in their relations to each other and in their behaviors in microscopical qualitative analysis. For pedagogical reasons a very brief outline of properties has been presented as an introduction to each "group" or "family" of elements or ions. These discussions are intended as mere summaries and rough generalizations, and like most generalizations are not always strictly accurate.

Such comparative studies are, however, particularly useful in connection with families of the elements according to the Periodic Classification, and exemplify some of the most beautiful relationships in the whole field of chemistry. The crystallographic similarity and interchangeability of chemically similar elements in compounds, embodied in the principle of "isomorphism," has been stressed whenever it has a bearing upon the reactions discussed, for it must constantly be borne in mind in microscopical analysis, and its importance is not sufficiently emphasized in our teaching of general chemistry.

CHAPTER I

MANIPULATIVE METHODS OF A GENERAL CHARACTER. HANDLING SMALL AMOUNTS OF MATERIALS

The manipulative methods or processes most frequently necessitated in qualitative analysis are:

- 1-Testing for solubility.
- 2-Bringing the material into solution; sometimes called "opening up the material."
- 3-Decantation.
- 4-Filtration or centrifugal separation.
- 5-Sublimation.
- 6-Distillation.
- 7-Fusions and ignitions.
- 8-Applying reagents.

1. Testing for Solubility and Heating Test Drops. — This is the preliminary step in all chemical analyses and should always be carried out in a thoroughly systematic manner.

At the corner of a scrupulously clean object slide place a small drop of water (or other solvent). Spread it out with a glass rod or platinum wire so that it occupies a circular area about 4 or 5 mm. in diameter and is about $\frac{1}{2}$ mm. deep. Closely adjacent to this drop (about 2 mm.) place a tiny fragment of the material to be tested.

Transfer the preparation to the stage of the microscope and focus upon the edge of the drop nearest the fragment to be tested. Use a low power and see that the illumination has been properly adjusted.

By means of a rod or wire or a stiff hair, slowly push the fragment into the drop of solvent, and study the preparation at once. Note well the phenomena which may take place. The substance may merely melt away; it may hydrate or form another salt; it may dissolve with decomposition and a precipitate may be formed; it may give off bubbles of gas; or it may remain unchanged.

If, after a few seconds, there appears to be no change in the size or in the appearance of the fragment of the material being tested, warm the drop

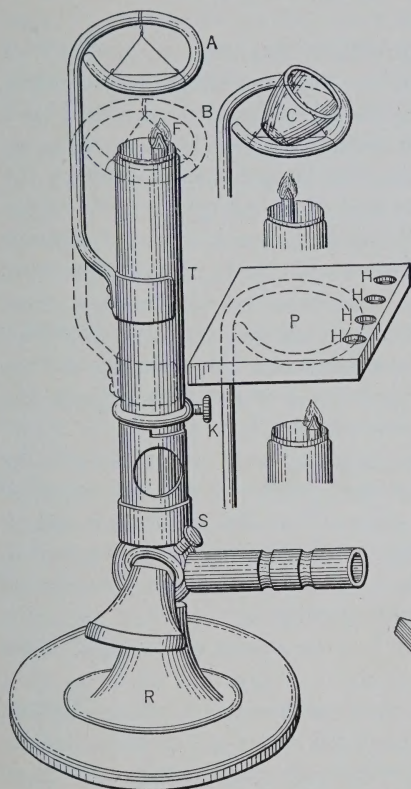


FIG. 1. Micro-burner with Support Ring and Hot Plate.

what larger test drop or a crucible. Tip the slide at an angle as shown in Fig. 2. Lower it so that the slide just barely touches the tip of the micro-flame and see that the heating

is done just under the upper edge of the drop. This precaution is necessary in order to prevent the drop from creeping up and spreading over the slide. Watch closely and as soon as bubbles are formed remove from the flame and *cool instantly* by

gently by holding it a second or two about one centimeter above a "micro"-flame. (F, Fig. 1. See also page 138, Vol. I.) The tiny flame should be so regulated as to be not over 5 mm. high. Cool the preparation quickly by bringing it in contact with a cool metal surface (base of the microscope or a metal block or plate). Examine the preparation and note whether there is now any change in the fragment indicating solubility in warm water.

Testing for solubility in boiling water requires a some-

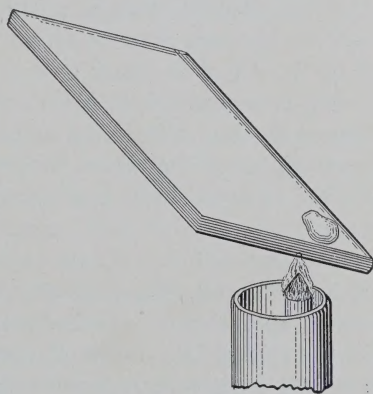


FIG. 2.

bringing the slide in contact with a cool metal surface. Unless this is done all the liquid will evaporate. It is essential to work quickly.

If the analyst is not restricted to very minute amounts of material, tests for solubility can be performed more conveniently in small crucibles and a drop of the solvent placed upon an object slide and evaporated for examination. When dealing with organic solvents having high volatility or low surface tension, the crucible method is preferable to that of operating upon the object slide. In all cases a "blank" should be made under conditions similar to the experiments performed upon the material in question, in order to eliminate the effect of possible impurities in the solvent.

Never place a hot slide upon the stage of the microscope, for the surface of the stage may be seriously damaged; moreover, vapors may arise from even moderately warm preparations and may condense upon the objective, injuring it.

If the tip of the micro-flame is brought into contact with the object slide, more or less lamp black is almost always deposited upon the under surface of the slide. This film must be wiped off with lens paper or a cloth before the preparation is examined. If this is not done fine details may be obscured or the color of reaction products may be misinterpreted.

Since the test drop was placed at the corner of the slide, there is no danger of breakage on heating.

To determine whether any material has passed into solution, decant the liquid from the undissolved material (see Decantation, page 8), and evaporate to dryness by gentle warming, being careful to avoid heating the preparation after it has gone to dryness.

It is impossible to obtain object slides made of glass sufficiently resistant that boiling water and acids will exert no marked solvent action upon them. Alkaline solutions will, of course, attack them in the cold. The results of tests for solubility should always be checked by comparison with the residues left when the solvent alone is evaporated under exactly the same conditions.

Tests for the solubility of substances in boiling corrosive liquids such as strong acids, alkalis, etc., should be performed on clean, bright platinum foil; the solvent should then be decanted, concentrated, and only transferred to a glass or silica or celluloid slide when evaporated almost to dryness.

Since illuminating gas usually contains appreciable amounts of various compounds of sulphur and ammonia, an alcohol lamp should be employed as the source of heat when "traces" of either sulphur or ammoniacal nitrogen are to be sought in material of unknown composition.

If the substance whose solubility is being tested is subsequently to be analyzed, a sufficient quantity of it is tested on glass, quartz or platinum, according to the necessities of the case, care being taken to observe the precautions given above, and to make a "blank" upon the water and reagent alone. A residue obtained by evaporation may not always be due to the action of the solvents on the glass but may result from impurities in the solvent.

When more than one solvent has been found, the proper selection will be governed by many circumstances. It is obvious that no rule may be given which will apply to even a majority of cases. Much must always be left to the judgment of the analyst.

Evaporating to dryness upon an object slide should be performed at a gentle heat only. Warm the preparation, then remove it from the flame and blow gently upon the warm drop; heat again, and again blow; repeat the process until the solvent has been driven off. If this method is followed, a uniform, closely adhering film will result instead of irregularly distributed loose particles, and the danger of loss through decrepitation of the tiny solid particles is avoided.

2. Bringing the Material into Solution. — When the solubility test shows that the material is practically insoluble in water, trials must be made to ascertain a suitable solvent. The fragment is tested with various possible solvents both cold and hot. HNO_3 and $\text{HC}_2\text{H}_3\text{O}_2$ are the most satisfactory from the point of view of qualitative analysis.

If silicates or analogous compounds are suspected and must be brought into solution for testing for cations, it is just as well to pass at once to HF , or to crystals of NH_4HF_2 and an acid. In such an event solution must be brought about on foil or in a cup of platinum, or upon a celluloid or cellulose acetate object slide, and care must be taken to observe all the precautions mentioned under Method X, page 43.

When alcohol or similar liquids of very low surface tension are used, it is more convenient to treat the material in a container such as a small crucible (Fig. 6, page 15) or a hollow slide, and

thus avoid the "creeping" of the solvent over the object slide. Holding the slide almost vertical reduces the creeping to a minimum, and if held in this position for a few seconds most of the volatile solvent will have evaporated and the drop of liquid remaining can be transferred to another inclined slide with little difficulty. The decanted drop usually creeps but little.

To ascertain whether alcohol or other analogous solvents have material in solution, it is often necessary to confine the evaporation to a small circular area in order that the residue may be studied. A satisfactory procedure is to take up the solvent in tiny tubes drawn down to hair dimensions. Touching these tubes to the liquid partly fills them by capillarity. A tiny drop is expelled upon a clean slide. Evaporation is so rapid, especially if the slide is slightly warm, that the drop cannot spread. When dry, another drop is forced out of the capillary tube and applied to the same spot as the first. The operation is continued until it becomes apparent whether any solvent action has taken place; the amount and character of the residue give the required information.

Many inorganic materials require treatment with concentrated acids or ammonium hydroxide or the fixed alkalis to bring them into solution. Preparations consisting of drops of strong HCl , HNO_3 , aqua regia, or NH_4OH should be placed upon the stage of the microscope for as short a period as possible so as to reduce danger of injury to the objectives. Preparations of this sort should be covered with a cover-glass, or the objective should be protected by a cover-glass held in place by a drop of immersion oil; or the device shown in Fig. 26, page 43, may be used.

When metals or alloys are to be brought into solution, care should be taken to dissolve them completely, and to test any non-metallic residue remaining. It is often sufficient to collect the sample by means of a ground glass slide, on which a "streak" is rubbed off. A drop of acid serves to dissolve the metal; the solution may then be decanted and tested further. By using a hollow slide, the concavity of which is roughly ground, more acid can be used and the solution can be carried out on a somewhat larger scale.² For filings or fragments of metals, a micro-crucible will be found indispensable.

3. Decantation. — The separation of a clear liquid from most precipitates or undissolved residues in as small volumes as single

² Strebing and Holzer: *Mikrochemie* 8, 264 (1930).

drops can ordinarily be accomplished without difficulty by decantation. Precipitates which float can be subjected to the treatment described below.

Success is largely dependent upon the use of object slides so scrupulously clean that a drop of water can be made to "wet" the surface of the glass and can be made to flow in a narrow continuous channel without breaking into a number of droplets. Object slides that do not permit the spreading out of a drop of water when stirred should be discarded, for the liquid cannot be satisfactorily drawn off if the surface of the slide is not free from an objectionable film.³

Hold the slide in a horizontal position. Carefully introduce the end of a drawn-out glass rod into the drop near the circumference. Draw the rod slowly and lightly across the slide, and at the same time slightly incline the slide in the direction of the path of the rod. Liquid will follow the rod in a narrow channel and, providing the movement is very slow, there will be little or no disturbance of the precipitated material. Having moved the rod for several millimeters from the test drop it is given a very slow circular motion, thus spreading the channel into a drop. This spreading out of the liquid upon the slide induces a flow from the test drop into the newly formed drop. The flow is facilitated by inclining the slide more and more and when the new drop is sufficiently large, or when practically all the supernatant liquid has been drawn off from the test drop, the rod is withdrawn. The preparation should

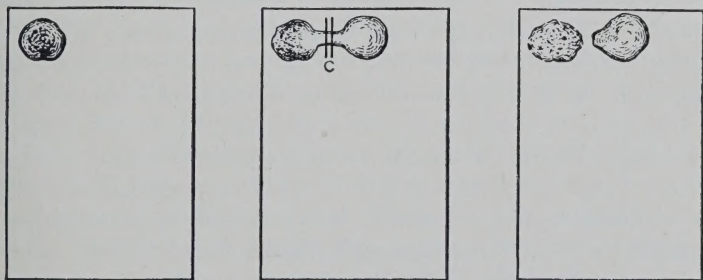


FIG. 3.

now consist of two drops connected by a narrow channel as shown in Fig. 3. A piece of folded filter paper is rapidly drawn across the channel C, Fig. 3, thus separating the two drops, and

³ For methods for cleaning object slides, see *Vol. I*, pp. 173-174.

the preparation heated gently at *C* over the micro-flame, to dry the slide at this point and thus prevent a back-flow of the decanted liquid. The slide can now be placed in a horizontal position, and either the residue in the test drop or the liquid in the decanted drop subjected to such further treatments as may be necessary.

The essential points to be observed are the proper angle of inclination of the slide, the rate and manner of spreading out the drop of the drawn-off liquid, and the cutting of the channel without absorption of too much liquid by the filter paper.

When an accumulation of solid matter forms a dam at the head of the channel and thus interferes with or prevents the flow of liquid, it is usually better to start a new channel to one side of the dam, for if breaking the dam is attempted the probability is that sediment will flow into the drawn-off liquid.

If the decanted liquid is not wanted for other tests, the decanted drop and connecting stream are wiped off the slide with filter paper, and the area they occupied warmed gently to dry it. It is frequently sufficient merely to introduce the edge of a thick piece of filter paper into the drop, removing the liquid by imbibition and simultaneously shoving the precipitate together into a small heap. This procedure is particularly convenient when decanting from a very small drop.

Not infrequently the suspended matter in the test drop persists in flowing over with the decanted liquid. When this occurs and heating the preparation is permissible, the following procedure may be adopted. Tip the slide so as to cause all liquid and suspended matter to flow back again into the test drop. Warm the preparation so as to dry the slide and prevent further flow of liquid. Evaporate the test drop to dryness by warming and blowing upon the preparation, carefully avoiding heating just as the drop becomes dry. Treated thus, the sediment generally adheres to the surface of the slide, and if a drop of water (or original solvent) is now carefully added the soluble materials will be dissolved, and the insoluble portion remains agglutinated and ordinarily adheres to the surface of the slide; decantation can then be practiced without much danger of a flow of sediment.

A precipitate is washed by adding to the test drop drops of water or other solvent and decanting after each addition and digestion.

When a number of drops are obtained in the process of washing,

and all of them must be saved and united for subsequent examination, it is best to transfer them to a second clean slide; this is done by decanting into the extreme corner of the slide, cutting off the stream with filter paper and warming as already described. Now slowly raise the slide to an almost vertical position and bring the corner, holding the decanted drop, in contact with the slide prepared to receive it. Touch the drop at the corner with a drawn-out glass rod or platinum wire and the drop will flow at once onto the slide below. Raise the vertically held slide and warm the wet corner over the micro-flame. Wash the residue as before and again transfer. The united washings may afterward be concentrated to the proper volume by evaporation.

In all cases where decantation is to be practiced the size of the drop to be treated should be somewhat larger than that employed in tests with reagents requiring no separation of liquid from solid.

The centrifuge is a useful aid in the decantation of relatively large quantities of liquid. (See *Vol. I*, page 147.) It has the advantage that separation of suspended matter is more complete, and that no precipitate is lost by becoming embedded in the surface of the filtering medium. Very minute quantities of liquid may be manipulated by means of the centrifuge, using tubes of 1–2-mm. inside diameter. The supernatant liquid can be pipetted out⁴ by means of a drawn-out capillary, and the precipitate can be washed repeatedly if desired.

4. Filtration. — The separation of a liquid from a precipitate is not always practicable by decantation. The solid may be so light or so finely dispersed as to refuse to settle out, or the turbid liquid may be contained in a receptacle such as a watch-glass or crucible or tiny evaporator. Under such circumstances recourse must be had to filtration.

The filtration of a drop upon an object slide is most satisfactorily accomplished by means of a filtration tube.⁵

A modification of the straight tube which we have found convenient is shown full size in Fig. 4, page 12. The lower end is ground smooth and true and exactly at right angles to the axis. To the upper end a piece of soft rubber tube about 80 mm. long

⁴ Emich: *Lehrbuch der Mikrochemie*, p. 44 (1926).

⁵ There appears to be some doubt as to the originator of the principle involved. It was in use by Behrens in 1898 and was described by Hemmes in 1898, *Rec. Trav. Chim. Pays-Bas* (II) **16**, 369.

is attached. See Fig. 5. The short piece of glass tube *M* serves as a mouthpiece. The filter tube is cleaned by pushing through it, by means of a stout brass wire, a plug of damp lens paper or filter paper.

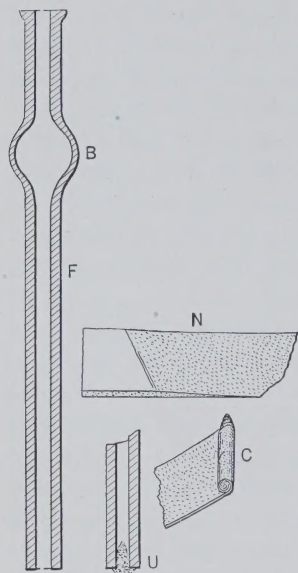


FIG. 4. Tube for Micro-Filtration.

than the diameter of the filter tube. The little square is conveniently cut upon a cork support with a very sharp knife, using a sawing motion so as to avoid unduly compressing the paper. It is then placed upon the object slide *S*, Fig. 5, which lies horizontally upon the table top, and the square is carefully moved until it occupies a position *P* closely adjacent to the drop to be filtered, *D*. The ground end of the filter tube is pressed lightly

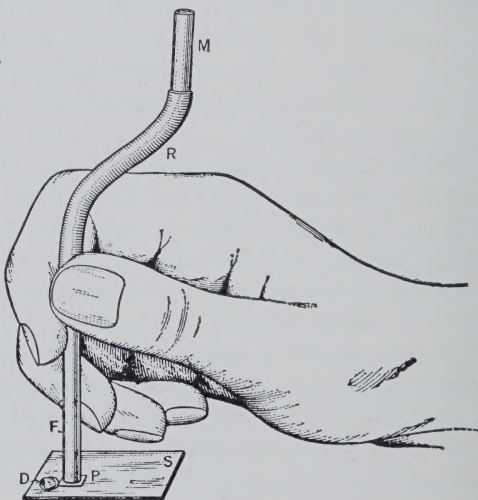


FIG. 5. The Behrens-Hemmes Method of Micro-Filtration.

but firmly against the filter paper in such a position that the paper projects slightly beyond the tube. The whole is then moved slowly forward into the test drop. As soon as the paper has become wet through, gentle suction is applied to the upper end of the tube by the mouth, through the agency of the rubber tube. At the same time the filter paper is slowly advanced still further into the drop; the precipitate, unless exceedingly fine, will be pushed along in a ridge before the advancing paper and the liquid will rise in the tube. Care must now be taken to keep the rubber tube slightly curved, as shown in the cut. When sufficient liquid has risen into the glass tube, suction is discontinued; the rubber tube compressed at its upper end between the fingers and is simultaneously straightened to prevent the forcing out of the liquid. To lift the tube from the slide and the piece of filter paper, stretch the rubber tube very gently and raise the whole apparatus.

The filtrate contained in the tube is removed by bringing the ground end in contact with a slide and bending the rubber tube, the upper end of which is kept closed; the liquid will generally flow out at once; if not, straighten the tube, open the upper end and blow *very gently*, but only just sufficiently to expel the drops.

A little practice is required to gauge the proper pressure of the tube upon the filter paper and to maintain this pressure uniformly without tipping the tube out of its vertical position, or pressing so hard as to make difficult the sliding forward of the tube and paper.

Too strong suction applied to the tube will cause the entrance of air, and there is then danger of sucking the liquid up into the mouth. This is particularly likely to happen if the test drop goes dry. The bulb *B* in the tube, Fig. 4, page 12, is designed to guard against this danger.

Unless the rubber tube is pinched and stretched just at the instant that the apparatus is lifted off the filter paper, the contents of the tube may flow back upon the slide.

Where larger amounts of liquid are available, or are contained in some vessel, and where a small loss of precipitate is of no importance, the filtering tube may be used in another manner. Savage⁶ has suggested the insertion of the filter paper into the

⁶ *Jour. App. Micros.* **3**, 678 (1900). The principle involved is very old. Filtering tubes with paper or asbestos fibers in their bore were advocated many years ago to filter volumes of about 1 cc.

bore of the tube. The same filter tube, Fig. 4, may be used. A long narrow strip of filter paper *N* is cut on a bevel as shown in the illustration and is rolled between the fingers into a rather tight, slightly tapering cigar-shaped plug *C* just large enough in diameter to fit snugly in the bore of the tube. When the unrolled portion of the paper strip is removed it should be done with a slanting tear so as to leave no ridge along the filter plug.

The long plug is inserted tightly into the tube, tapering end up. It should have not over 4 to 6 mm. within the tube. The projecting part is cut off about 1 mm. from the end of the tube, using a sharp knife with a sawing cut against cork. The projecting end is then "upset" with the knife blade as shown in Fig. 4, *U*, page 12.

The plug is first moistened with the same sort of liquid as is to be filtered and is dipped directly into the test drop. Suction is applied by the mouth through the rubber tube. The clear liquid rises in the tube. When sufficient filtrate has been obtained suction is discontinued and the tube lifted out of the test drop.

The filtrate can be removed by means of a capillary pipette, after disconnecting the rubber tube or, better, by pulling out the filter plug with a pair of forceps while holding the tube in an almost horizontal position, and expelling the liquid against an object slide by compressing the rubber tube.

Instead of paper, a rolled plug of asbestos or other fibrous material can be employed.

The plug filter has the advantage that little manipulative skill is required in its use and that it is applicable to the filtration of liquids contained in watch-glasses, crucibles, evaporators, etc. But, on the other hand, considerably larger volumes of liquid are required than when using the Behrens-Hemmes method.

The authors have found in certain instances that "Alundum" filters have proved of great value. Such filters are made by grinding tiny conical plugs from pieces of broken "Alundum" crucibles and fusing these plugs into the ends of glass tubes 2 to 2.5 mm. in diameter and 50 to 60 mm. long. After fusing, exceptional care must be taken in cooling and annealing. In like manner porous porcelain plugs may be used, but in such an event a powerful suction pump is required, suction by means of the mouth being insufficient to cause the passage of the liquid. With care in fusing the glass to the porcelain tiny germ-proof filters are thus obtained.

Centrifugal separation (see *Vol. I*, page 147) is a valuable substitute for filtration, both because of the avoidance of loss of precipitate on the filtering medium and because strongly corrosive liquids, which would attack paper or asbestos, can be handled. By inserting a tiny filtering tube within a centrifuge tube of ordinary size, centrifugal force may be used as a substitute for suction.⁷ The centrifuge is particularly useful in clearing viscous liquids.

5. Sublimation.—The methods and apparatus for separations and analyses by sublimation have been discussed at length in *Vol. I*, pages 348–354. The simplest procedure consists of subliming from one object slide to another (*Vol. I*, page 349).

One form of apparatus which the authors have found to be especially useful is again figured (Fig. 6) since it will be frequently referred to in the present volume in the discussion of qualitative tests for both cations and anions.

In inorganic qualitative analysis the sublimation of oxides and chlorides is more conveniently performed by heating on platinum, tantalum or nickel spatulas (Fig. 19, page 24). The sublimate is collected on silica or "Pyrex" object slides, or if care is used the sublimate can be condensed upon object slides of ordinary glass.

When a very small amount of material is to be handled sublimation in a drawn-out capillary tube, preferably of hard glass, prevents losses (Fig. 27, page 44).

Difficultly volatile substances, such as metallic oxides, may be sublimed on charcoal or plaster of Paris by means of a blowpipe to give coatings which have characteristic appearances.

6. Distillation.—Fractional as well as simple distillations can be successfully performed on a "micro" scale and the separations

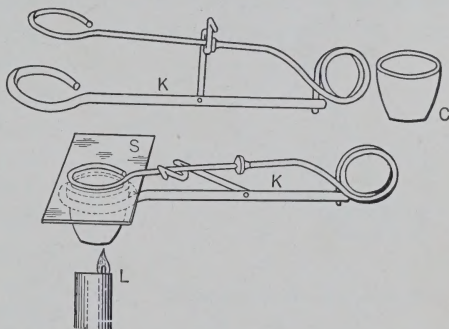


FIG. 6. Apparatus for Micro-Sublimation, Micro-Distillation, and Gas Evolution. K — spring clamp. C — glass crucible. S — object slide. L — micro-burner. ($\frac{1}{2} \times$.)

⁷ Emich: *op. cit.*, p. 47.

effected are usually sufficiently sharp for the purposes of qualitative analysis.

Fractional distillations with temperature control are, however, rarely practicable on a "micro" scale. The results obtained do not ordinarily warrant the time and trouble involved in the setting up and the operating of complicated apparatus and the acquiring of the requisite technique.

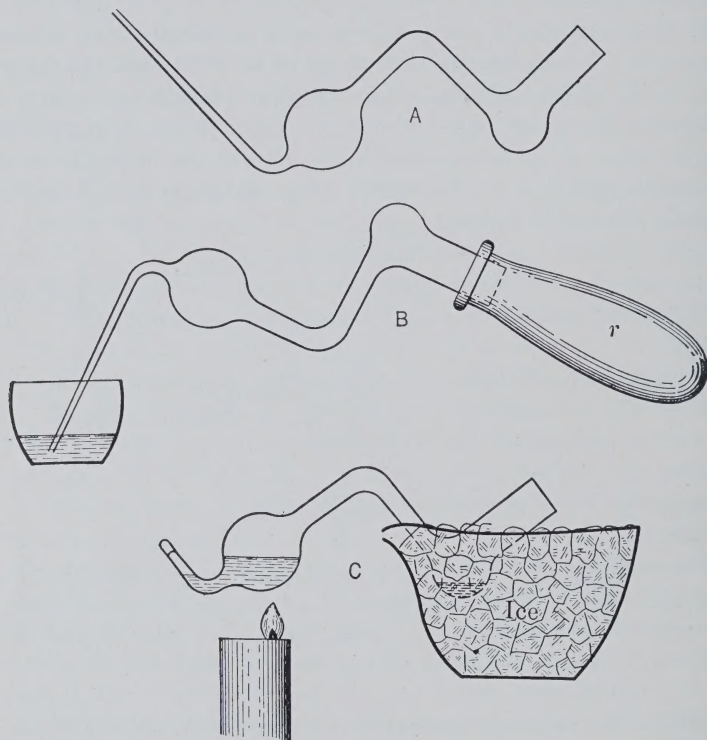


FIG. 7. Fractional Distillation of a Volatile Liquid.

The micro-distillation apparatus and methods which have been described are many and varied.⁸ In the present Handbook the authors have confined themselves to a discussion of those methods only which are in use in their laboratories.

⁸ Behrens-Kley: *Mikrochemische Analyse*.

Emich: *Mikrochemische Praktikum* (1931) p. 33, *Lehrbuch der Mikrochemie* (1926) pp. 56, 123.

Benedetti-Pichler: *Fortschritte der Mikrochemie in den Jahren 1915-1926*, p. 176.

For fractional distillation of volatile liquids, small distilling tubes can be employed and satisfactory results obtained. A convenient form is shown in Fig. 7,⁹ page 16. To introduce the liquid to be distilled, a rubber pipette cap *r* is slipped over the large end of the tube (Fig. 7 *B*); the tube is inverted as shown and the liquid drawn into the bulb in sufficient volume to fill not quite half of it. The tube is then again turned to the position *A*, the bulb containing the volatile liquid is surrounded by ice (or a freezing mixture), and the drawn-out tube sealed off in the flame of a blast lamp or blowpipe. The bulb is removed from the ice, wiped dry and the apparatus arranged as shown in Fig. 7 *C*. The liquid may now be heated, and the successive fractions which condense, removed with a pipette drawn down to a fine tube having a slightly curved end. (See *Vol. I*, page 143, Fig. 71.)

If the compound to be distilled must first be set free by the action of some reagent, the tube shown in Fig. 8 is to be preferred. Ma-

terial and reagent are introduced through the side arm, which is then closed with a tiny plug of soft wood or cork, or by fusion. Condensation is obtained by winding the narrow inclined tube with filter paper or cloth wet with cold water or a volatile

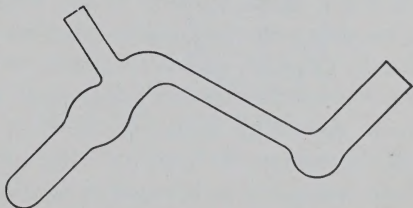


FIG. 8. Tube for Micro-Distillation.

non-flammable liquid. If the distillate is quite volatile the receiving bulb should be surrounded by ice, as shown in Fig. 7. When temperatures of vaporization are required the bulb containing the liquid can be introduced into one of the hot stages shown in *Vol. I*, Fig. 88, Fig. 90, or into an oil bath.

Distillations involving no fractionations can be successfully and more conveniently performed in the apparatus shown in Fig. 6. It consists of a container *C* which may be of glass, quartz, porcelain or metal. The rim of *C* is ground smooth and true so as to fit hermetically against an object slide *S* when in use. The clamp and holder *K* serve to support the container and to hold the cover tightly in place during the heating. To keep the condensing surface cool a large drop of water can be placed upon the upper sur-

⁹ This is essentially a modification of Behrens' double-bulbed tube, but is somewhat more convenient. Emich has described a closely similar modification.

face of the slide within the upper ring of the clamp, or better, a cooled cylinder of silver, aluminum or copper can be placed within the ring. A cylinder 1 cm. high and of a diameter to fit easily within the upper ring serves as a very efficient cooler, especially if a cup-shaped depression is made in the upper end and in this depression a little chloroform, carbon tetrachloride or other very volatile non-flammable liquid is placed.¹⁰

The procedure in a distillation is as follows. Place in the container the material to be treated. Lay over it a tiny bunch of fibrous asbestos which has just been ignited to redness by being held with the forceps in the flame of a Bunsen burner. In the absence of asbestos, pure glass wool or in certain cases even a piece of filter paper may be employed as the absorbent, but if filter paper is employed a blank must always be made to prove that no misleading substances result. The asbestos or glass wool prevents the spurting and splashing of the liquid. Upon the absorbent is placed a small amount of the material to be tested. Invert a glass slide over the container thus prepared. Clamp the cover-slide firmly in place, and heat gently over a micro-flame until a sufficient condensation has taken place upon the slide. The clamp is then opened by means of the lever and the slide carefully lifted off the container *C*, turned over and the condensate subjected to such treatment as is required for its identification.

Although the device just described may be applied to the fractional distillation of small amounts of volatile liquids, the distilling tubes described above will be found better adapted to this sort of work.

7. Fusions are performed in depressions made in platinum, silver, or nickel foil or in tiny vessels of metal, silica, or porcelain, or hemispherical depressions are hollowed out in a block of carbon or graphite and material fused therein by means of a blowpipe.

Satisfactory cups for very small amounts of material can be readily stamped in thin platinum foil. A brass or bronze rod is shaped to conform with the size and style of cup desired; it is then hammered into a block of lead. This gives a die by

¹⁰ Conversely, when subliming compounds with a high subliming point, it is often advisable to keep the object slide warm in order to induce the formation of larger and better crystals. Gas-carbon or graphite cylinders, previously warmed, hold their heat for a sufficient period to enable the analyst to obtain excellent sublimates upon the cover-slide, (*e.g.*, As_2O_3).

which tiny cups can be rapidly and inexpensively made. Fig. 9, shows block, plunger, and cups of different depths. It is convenient to prepare a block of lead with depressions of different depths, thus providing for fusions of varying amounts of material. After the fusion has been completed, the fused mass removed, and the "cup" cleaned, it can be reshaped by laying it in the die and giving it a slight tap with the plunger and a small hammer. For larger amounts of material the platinum cups shown in Fig. 10, will prove useful.

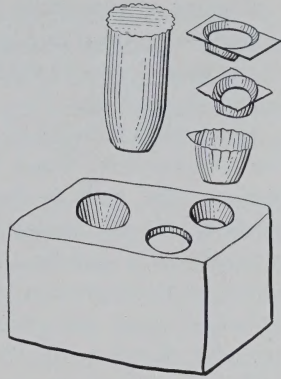


FIG. 9. Block and Plunger for making Foil Cups.

All cups or foils are handled by means of forceps, but when blowpipe fusions must be practiced, compression

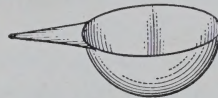


FIG. 10. Platinum Cups for Fusions. (Full size.)

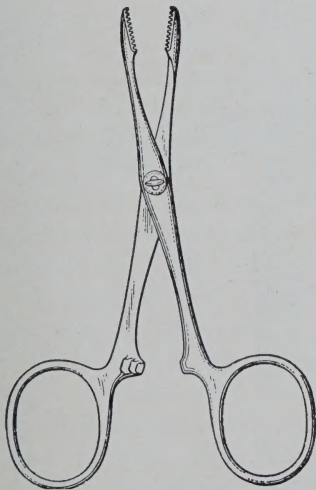


FIG. 11. Surgical Compression Forceps. Convenient for Holding Small Cups or Pieces of Foil.

forceps of the type shown in Fig. 11, are a great convenience, because they can be locked shut, thus relieving strain on the fingers during a long

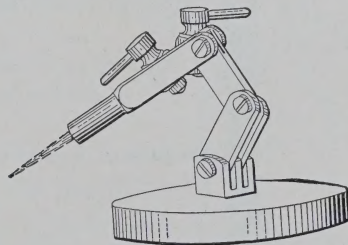


FIG. 12. Grunberg Orthodontic Blow Pipe $\times \frac{1}{2}$. (S. S. White Dental Co.)

fusion, and eliminating the danger of dropping the bits of foil or tiny cups.

For blowpipe fusions the Grunberg

Orthodontic Blowpipe (Fig. 12, page 19) will be found exceptionally convenient.

Fusions at Bunsen burner temperatures are made over burners of the type shown in Fig. 1, page 5. The platinum wire triangle in the ring *A* can be readily bent so as to support the cups shown in Fig. 9, page 19.

The fusing mixture is placed in the "cup," heated slowly and the temperature raised until it has been brought to complete fusion. The melt is then removed from the flame and a tiny fraction of the material under investigation is added. The preparation is then heated to complete fusion, a second portion is added and the process kept up until sufficient material has been added to meet the requirements of the analyst. In the great majority of cases this fractional addition is preferable to that of adding the whole amount at once, for the progress of the reaction is more readily followed.

Fusions with Na_2CO_3 and KNO_3 are best made in platinum, those with NaOH , KOH or Na_2O_2 in silver, those with KOH and KClO_3 in porcelain. Metals and alloys can be fused on carbon using a suitable flux to prevent oxidation.

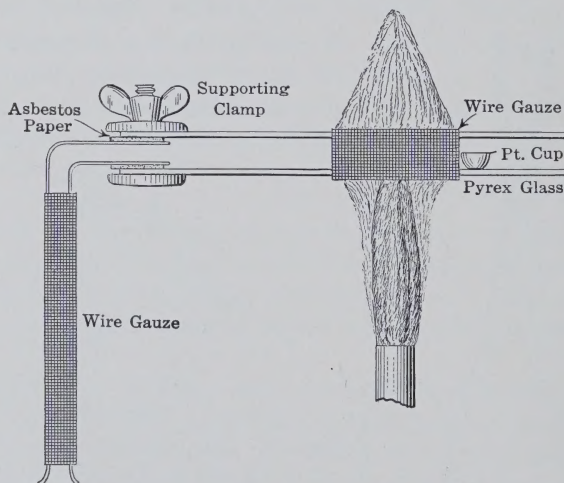


FIG. 13. Pregl Type Muffle for Micro-Ignition.

Very small amounts of material may conveniently be subjected to fusion in a bead contained in a platinum loop. A blast lamp

of the type shown in Fig. 12, page 19, or a mouth blowpipe may be used, with either an oxidizing or a reducing flame. Color reactions in the melt, and suspended or skeletal material in the bead, may be observed as guides to chemical testing.¹¹ Borax, or "microcosmic salt" ($\text{HNaNH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$) are the most commonly used fluxes. The platinum loop can easily be cleaned by breaking off the bead, and then by "rinsing" with successive beads of fresh flux.

Ignitions are performed in the manner usually employed in quantitative work, but to avoid possible losses through convection currents it is better to carry out the heating in some type of muffle which may be either gas or electrically heated. Fig. 13, page 20, illustrates a type of tiny muffle furnace that is easily made of hard glass (or better of fused silica) and will be found practical and efficient.¹²

8. Reagents and their Application. — Since the reactions employed in microscopic qualitative analysis are extraordinarily sensitive, unusual care must be taken to avoid contamination of reagents. Liquids and solutions kept in small bottles for convenient use should be frequently renewed, since they soon become contaminated by foreign material, derived from the containers. As many reagents as possible should be kept in the solid state rather than in solution. One of the most serious sources of contamination is "dust" from the air falling about the stopper of the bottle and finding entrance into its contents whenever the stopper is removed.

Acids, distilled water, and solutions in constant use are conveniently kept in bottles of the type shown in Fig. 14.

A practical and wholly satisfactory system for reagents frequently required in qualitative analysis is that due to Behrens (Fig. 15, page 22). It consists of a box housing 60 or more 1 cc. glass-stoppered vials. When not in use the cover protects them from dust and dirt. Or we may use a simple block to hold the vials

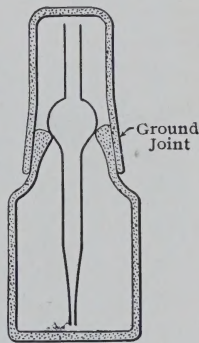


FIG. 14. Dropping Bottle with Pipette and Cap. $\times \frac{1}{2}$.

¹¹ Moses and Parsons: *Mineralogy, Crystallography, and Blowpipe Analysis*. Kraus and Hunt: *Mineralogy* (1928) Chap. XV.

¹² Pregl-Fyfe: *Quantitative Organic Microanalysis*, p. 165 (1930).

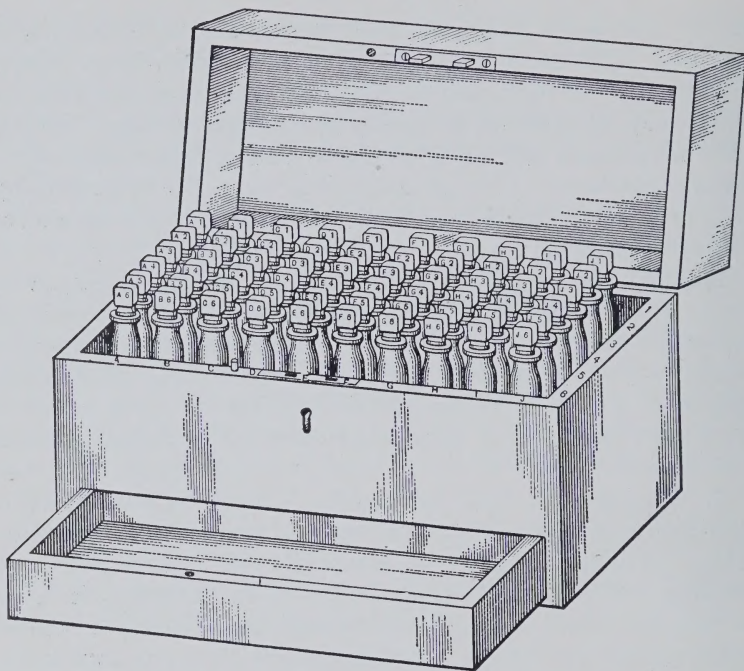


FIG. 15. Reagent Set for Microchemical Analysis. (Behrens.)

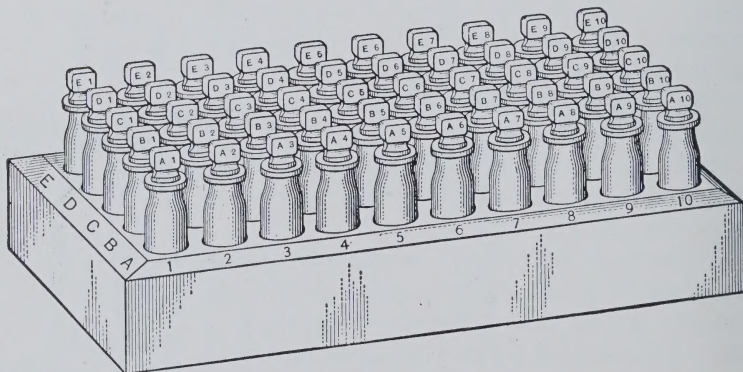


FIG. 16. Wooden Block with Small Vials for Reagents.

(Fig. 16).¹³ A chart giving a list of the reagents required in the routine analysis of common inorganic compounds will be found on page 401.

¹³ Such a set of reagents can be obtained from the Will Corporation, Rochester, N. Y.

A number of reagents, even in the comparatively dry state in which they are placed in the vials, attack the glass and become seriously contaminated. An excellent example is afforded by uranyl acetate. This salt takes up sufficient sodium in a short time to render it unfit for use. To prevent this deterioration the vials can receive a coating of ceresin or other suitable wax, or a coating of varnish, or a small cylinder of paper with twisted end can be inserted in the vials.

Ammonium fluoride can be kept in tightly stoppered ebonite tubes having stoppers as shown in Fig. 17, or the tubes can be fitted with ordinary soft rubber stoppers. Ammonium fluoride of commerce is unfit for micro-analyses unless it has been carefully resublimed in platinum. This can be done by heating in a platinum dish and condensing the vapors upon the under side of another platinum dish filled with cold water. The operation must be conducted in a hood.

All reagents should be tested for their purity by performing "blank" tests. In this connection it must not be forgotten that practically all the rubber goods of commerce contain a considerable quantity of "filler" which is readily soluble in acids and other liquids. It is therefore important that contact of reagents with

rubber should be avoided as much as possible. The most frequent cause of trouble is zinc in the reagents derived from the zinc oxide used as a filler; red rubber often contains antimony sulphide.

Reagents can be handled by means of drawn-out glass rods, or platinum or tantalum wires

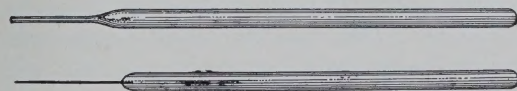


FIG. 18. Drawn-out Glass Rod and Platinum Wire for handling Reagents.

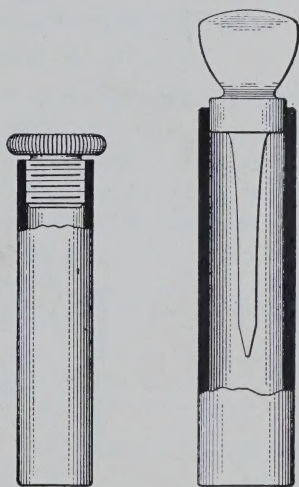


FIG. 17. Ebonite Tubes for Ammonium Fluoride.

fused into a glass handle. (Fig. 18.) If about 1 mm. of the very tip of the rod is slightly roughened with HF or by rubbing

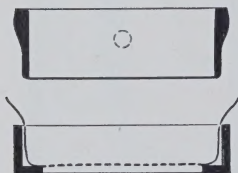
with a piece of abrasive cloth or paper it will pick up both solids and liquids better. To pick up solids the end of the tube or wire is breathed upon and then immediately applied to the powdered material; several particles will adhere and can be transferred to the drop to be tested. Simply dipping into a liquid and withdrawing without touching the neck of the container will ensure that a drop of the liquid will cling to the glass or wire.

For transferring larger amounts of material, a small platinum spatula is indispensable. (Fig. 19.) It is made from a piece



Fig. 19. Platinum Spatula. (Full size.)

of hard drawn platinum wire about 1 mm. in diameter and 80 to 85 mm. long; one end is hammered flat upon a polished steel surface until it becomes a little over 3 mm. wide and the flattened surface about 10 mm. long. The blade is then shaped with a file, smoothed and polished. The opposite end of the wire is given a blow or two of the hammer and filed to a double chisel edge and polished. This end is used chiefly for loosening reagents in vials and for breaking up fragments of soft or friable salts.



Odds and ends of glass rods and glass tubes drawn down in the blast lamp to less than 1 mm. in diameter and cut into lengths of about 60 mm. make excellent carriers of reagents. After use they are thrown away.

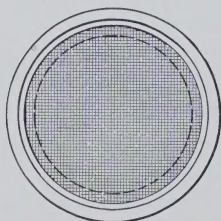


Fig. 20. Sieve of Silk Bolting Cloth. (Full size.)

It is often necessary to screen small amounts of material. This can be accomplished by means of silk bolting cloth of suitable mesh size. The cloth is stretched in a tiny metal frame constructed upon the principle of embroidery rings, as shown in Fig. 20. After use the cloth is removed and thrown away.

The various methods for applying reagents are discussed in detail in Chapter II.

In all discussion of tests in this Handbook the authors have made use of certain terms which need a few words of explanation.

Test Drop. — The drop of solution containing the material to be tested. Unless otherwise specified, this drop is supposed to be spread out upon the object slide over a circular area about 6 to 7 mm. in diameter and to be not over 1 mm. deep at its center. Smaller drops may be used if desired, but they are likely to be so highly curved as to prevent observation of precipitates within them.

Reagent Drop. — The solution of the reagent; a drop of approximately the same volume as that of the test drop. If this drop is placed upon the object slide and caused to flow into the test drop it should not be spread out in a thin layer but should be almost twice as deep as the test drop.

Inner Zone of Precipitate. — The relative position shown at *i* in Fig. 21.

Outer Zone of Precipitate. — The relative position shown at *o* in Fig. 21.

Concentrations are in general discussed in terms of the *size* of the fragments of unknown and reagent and may be indicated thus, for substances readily soluble in water:

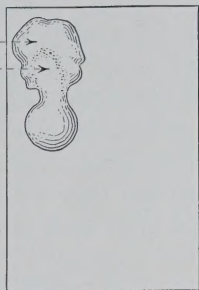


FIG. 21.

<i>Very dilute,</i>	a fragment the size of this dot (·)
<i>Dilute,</i>	“ “ “ “ (•)
<i>Moderately concentrated,</i>	“ “ “ “ (●)
<i>Concentrated,</i>	“ “ “ “ (●)
<i>Very concentrated,</i> a practically saturated solution.	

It will be obvious that any such arbitrary designations of concentrations cannot be applied to difficultly soluble compounds, and can serve merely as a rough guide of relative values. These designations have been used because of the criticism that has not infrequently been made that authors of microchemical tests use the terms *concentrated* and *dilute* with no explicit statements. Per cent concentrations are impractical since it is impossible to estimate weights and volumes when dealing with such small quantities, and when dealing with unknown materials and mixtures there is no knowledge as to compositions.

Sensitivity of Reactions. — It is perhaps unfortunate that in the past so much stress has been laid upon the sensitivity of micro-

scopic chemical tests, both because their advantages of ease and directness are thereby obscured, and because the impression is given that they are appropriate only in case extremely minute amounts of material or low concentrations are to be dealt with. Actually, of course, a chemical reaction involving the formation of a precipitate will give a positive result whenever the "solubility product" of the precipitate is exceeded, whether the reaction is carried out in a drop or in a test-tube. Since the great majority of reactions used in microscopical analysis are also employed in ordinary macroscopic analysis, it is evident that, in terms of concentrations of the reacting solutions, no increased sensitivity can result. Furthermore, these reactions are usually at a distinct disadvantage when applied as microscopical tests, and in most cases are unsatisfactory at dilutions distinctly less than those which correspond to the solubility of the precipitate. This is due to the fact that the *effective* "solubility product" of a given precipitate may vary greatly, depending upon the presence of other ions (not necessarily "common ions") and the formation of complex ions. In addition it must be borne in mind that macroscopic tests are ordinarily carried out in solutions which have been subjected to preliminary separations, whereas microscopical tests are usually made in the presence of whatever other substances happen to be in the unknown solution.

The factors which often govern the choice of a reagent for microscopical tests may be directly at variance with the chief considerations in macroscopic tests. Definitely crystalline precipitates are sought in microscopical analyses in order that their form and optical properties may serve to identify them. Distinctive crystals are not ordinarily obtainable by the precipitation of highly insoluble substances such as those on which most macroscopical tests are based. Consequently there is frequently a deliberate sacrifice of sensitivity, by the choice of a reagent which will give a relatively soluble precipitate in recognizably crystalline form, instead of one which will yield an apparently amorphous precipitate at extreme dilutions. The use of Ca^{++} instead of Ba^{++} in testing for SO_4^{--} is a good example of this. Occasionally the conditions under which the test is made are purposely altered in the direction of a reduction of sensitivity, so as to obtain a more characteristic precipitate; for example, in the precipitation of Ag_2CrO_4 or PbI_2 from slightly acid solution.

The apparent sensitivity of microscopical qualitative reactions is increased by a number of factors. The material to be tested appears, in the solid state, to be exceedingly minute. It must be remembered that the solvent is used in correspondingly minute quantity, so that actually the solution may be fairly concentrated. The reagent, especially when added as a solid, is commonly present in concentrations which may approach saturation. A drop of the unknown solution, too dilute to give an immediate precipitate, may yield crystals on standing or warming, due to evaporation and concentration of the solution.

The influence of the various factors mentioned above renders any numerical expression of the sensitivity of a reaction of somewhat questionable value, since it may be subject to so many influences. As a means of indicating roughly the relative limits of different tests, such data may be useful, but a negative test should never be interpreted as indicating that the actual concentrations or quantities of the material sought are less than the reported sensitivity.

Sensitivities of reactions may be expressed in various ways:

1—As the limiting concentration, in grams per liter or cc., or μ g. per drop of definite volume, at which a definite positive test is obtained.

2—As the minimum amount of material which will yield a positive test.

3—As the minimum per cent of material in the presence of another material, from which a positive test may be obtained at a given dilution.

The first method of stating sensitivities will, of course, be related to the second, if the amount of solution employed is known. This may range from several drops (say 0.2 cc.) to one drop (ordinarily about 0.02 cc.). If the solution to be tested is concentrated further, before the test is applied, the limiting concentration in the original solution may be very much less than if this solution were tested directly. The advantage of such procedure, when several drops of a highly dilute solution are available, is obvious, but a "blank" should be run to eliminate the effect of an impure solvent. The limits of sensitivity should also, if possible, be stated for different mixtures of materials, especially in cases where

the test is commonly employed to detect small amounts of one substance in the presence of another.¹⁴

Character of Precipitates. — A precipitate has been designated as “**amorphous**” when a magnification of 200 to 300 $\times$ fails to disclose any fine crystals, but merely flocs or curdy or gelatinous masses; it has been called **granular** when it consists of dispersed particles so fine as to appear as dots only; if these dots can be resolved into more or less spherical grains under a magnification of 150 or 200 $\times$ the precipitate has been called **sandy** or as consisting of granules.

The photomicrographs illustrating the various tests are roughly representative of the size of the crystals obtained, at the magnifications indicated. However, since the fineness of a precipitate can vary over wide limits, depending on the concentrations of the reacting substances, temperature, digestion, etc., the dimensions of crystals cannot be used as a positive criterion for differentiating between substances having similar form.

¹⁴ Discussions of the sensitivity of microscopical reactions, and methods of expressing it, are given by:

Behrens-Kley: *Mikrochemische Analyse* (1921) p. 31.

Feigl: *Mikrochemie* **1**, 4 (1923).

Emich: *Lehrbuch der Mikrochemie* (1926) pp. 3, 7.

Hahn: *Mikrochemie* **8**, 75 (1930).

Heller: *ibid.* **8**, 141 (1930).

CHAPTER II

METHODS OF APPLYING REAGENTS IN MICROSCOPICAL QUALITATIVE CHEMICAL ANALYSIS

In order that characteristic tests which are always dependable and readily interpreted may be obtained, it is essential that the analyst shall bring about a given reaction under definite and reproducible conditions.

Most of the "micro" tests available for the detection of ions, complexes or compounds are dependent upon the separation of a crystalline phase which possesses a constant crystal habit peculiar to the substance being sought.¹

To bring about the proper conditions which shall assure a rapid and certain reaction requires that a given test shall be performed always in the same manner and under the same conditions, for we require not only a definite reaction product but also one which shall separate always with the same crystal habit, and form crystals of approximately the same size whenever the test is made.

The necessity of controlling the conditions under which the reaction product is formed will be even more obvious if it is recalled that many compounds exist in two or more forms. Some of these forms are unsatisfactory as reaction products upon which to base an opinion, and it is necessary so to perform a test as to insure the separation of the proper phase.

Under similar conditions as to concentration of substance and reagent, acidity or alkalinity, temperature and manner of reagent application, the crystalline phase will not only separate with always the same habit, but the majority of the crystals will usually develop to the same size and will lie on the same faces upon the object slide, in each separate experiment.

In order that a test may prove satisfactory and conclusive, the solid crystalline phase desired should separate almost immediately. If long in forming, evaporation takes place and it is highly probable that other crystalline compounds may then separate and

¹ See *Vol. I*, Chap. X.

thus mask the test. On the other hand, conditions leading to the instantaneous precipitation of the identifying reaction product usually force it to separate in such a finely dispersed state, or in such non-characteristic skeletal forms, as to render the test of questionable value.

Method I: A drop of a solution of the reagent is caused to flow into a drop of the solution of the material to be tested. — This method of adding the reagent to the test drop is of general applicability and can be employed in practically all micro tests made upon object slides. By its use the quantity of reagent brought into reaction with the unknown ions is more readily controlled than is possible by other methods, and there are fewer complications in the interpretation of the phenomena produced.

Preliminary tests with a given reagent are best made by this method, and from the results obtained the most satisfactory method of reagent application can be properly judged.

Near the corner of a scrupulously clean slide (see page 9), place a drop of a solution of the material to be tested. Spread the drop with a glass rod or platinum wire until it attains a diameter of about 5 to 7 mm. and a depth of less than 1 mm. This drop will hereafter be called the test drop.

A drop of the reagent solution of a diameter of approximately 5 mm. is next placed close to the test drop, but not touching it. The concentration of the reagent drop should (save in very exceptional cases) be slightly greater than that in the test drop, or, to be more exact, the density of the reagent drop should be sufficiently greater than that of the test drop to insure the reagent solution sinking into the liquid of the test drop.

By means of a drawn-out glass rod, or by means of a platinum wire, a tiny channel is made to flow from the reagent drop into the test drop, the object slide being tipped very slightly to facilitate the flow, but under no condition should the two drops merge. Care should be observed, when introducing the reagent into the test drop, not to rub the glass slide with rod or wire, otherwise too rapid crystallization may result.

Crystals formed upon the slide have their more perfectly developed faces on the upper side and can be more easily studied. Floating crystals, supported by surface tension, grow downward into the liquid and as they grow and become heavier they tend to sink deeper; the upper side alone can be studied, and as this is al-

ways irregular, malformed, and seldom transparent, the true habit of the crystals may not be distinguishable or may be misinterpreted.

When the reagent is properly added the preparation should appear as shown in Fig. 21, page 25.

As the reagent enters the test drop, the formation of the reaction product creates a dam or hinders the direct flow of the reagent solution, the velocity of the further reaction is checked, and at some point where the channel enters the test drop concentration conditions will exist favorable for the growth of well-formed characteristic crystals of the product sought. This favorable condition may be in the outer zone *o* or in the inner zone *i*.

In very rare cases better results appear to be obtained by causing the solution of the substance to be tested to flow into the reagent drop.

Typical Applications:

See Potassium, Method A, page 66.

Zinc, Method A, page 124.

Method IA: A drop of the reagent is added directly to the test drop at its center. — This method is applicable to all reactions not requiring careful control of concentrations, or, in other words, tests in which the reaction product will invariably separate under wide variations of conditions.

The usefulness of the method is usually restricted to adjustment of acidity or alkalinity; to precipitations where the crystal form is immaterial and a solid phase is produced for the purpose of separating it from other compounds, in order that tests of some sort may be subsequently applied to it, or to the solution from which it has been eliminated. It is also successful where a solution of exact strength is added to a test drop of known concentration. In all other cases Method I is to be preferred.

Method IB: Reactions in capillary tubes. — Reactions can be carried out in capillary tubes, the resulting precipitate being observed under the microscope. Glass tubing, carefully cleaned and drawn out to about 2-mm. inside diameter, is cut and sealed off to give lengths which are used just as are test-tubes.²

² Fuchs: *Monatshefte* **43**, 129 (1922).

Emich: *Mikrochemisches Praktikum*, 2 Auf. (1931) p. 25.

Lehrbuch der Mikrochemie (1926) p. 44.

Hahn: *Emich Festschrift, Mikrochemie* (1930) p. 143.

As an illustration of this technique, see Benedetti-Pichler: *Ind. Eng. Chem. (Anal. Ed.)* **2**, 309 (1930).

Volatile liquids can be handled with little loss, and warming or digestion can be carried out with less evaporation than from a drop on an object slide.

For transferring liquid from one capillary tube to another, and for separating precipitates, the centrifuge is convenient. Pipettes made from tubing drawn down to 1-mm. or less outside diameter are useful for drawing off supernatant liquids, collecting sediments, introducing reagents, etc.

Method II: A fragment of the solid reagent is added to a drop of the solution to be tested. — This method is designed to insure the presence of an excess of the reagent at the very beginning and during the early progress of the reaction. It is of special value when the reaction product is a double salt in which the reagent must be present in the greater ratio, or when two double salts are possible (*e.g.*, $3 \text{ CsCl} \cdot 2 \text{ BiCl}_3$ and $3 \text{ CsCl} \cdot \text{BiCl}_3$) and it is the salt with the larger proportion of reagent that is desired; in such cases a large fragment of the reagent is added at the center of the shallow test drop. The preparation must not be stirred.

The size of the reagent fragment should be such that its upper surface shall be at the surface of the drop, or better, just barely above it. The reagent dissolves at a very high concentration, and sinking into the less concentrated test drop causes convection currents to bring the material to be tested in contact with an almost saturated solution of the reagent.

It not infrequently happens that in the disintegration and solution of the reagent fragment a saturated solution of the reagent results in a zone about the fragment, and as a consequence crystallization of the reagent itself takes place. The inexperienced analyst may thus be misled and mistake these crystals for a compound formed by the reagent with some salt present in the test drop. This source of error can be avoided if the crystal habit of the reagent has been previously studied. Another puzzling phenomenon, occasionally observed, is that of the temporary formation of a compound in a zone in contact with the reagent fragment, and the almost instantaneous disappearance of the crystals as they drift beyond the zone of high concentration. Hydration of dehydrated reagents, or the decomposition of one which is a double salt (for instance, $\text{K}_2\text{Hg}(\text{SCN})_4$), may result in such apparent anomalies.

Method II is unsuited to reactions in which the reaction product is very difficultly soluble or is curdy or flocculent, for under such

conditions the reagent fragment becomes immediately coated with an almost impenetrable phase and the reagent cannot dissolve and enter into a further reaction. Under conditions such as these Methods I or IA must be resorted to.

Method II will be found a safe procedure in most reactions where the reaction product first formed is soluble in excess of the reagent, for the analyst wishes to see the solid phase formed by the reaction and also observe its solubility in an excess of the reagent.

Adding the solid reagent provides for both precipitation and subsequent re-solution. There is always an appreciable time, owing to the slow solution of the reagent, during which there exists a zone where the concentrations are such that the solid phase of the reaction product can exist. Thus the fragment of the reagent will be surrounded by a clear ring or zone at the outer edge of which the solid crystalline phase may be easily seen under the microscope. If the fragment of the reagent is too large or dissolves too quickly, the zone of solution may increase so rapidly that it reaches the circumference of the test drop before the analyst has time to note the formation of the transitory solid reaction product.

The fragments of the solid reagent added should always be dense and compact, so as to insure its gradual solution; for if it is in fine powder and of such loose texture that it disintegrates, it will dissolve almost instantly when added to the test drop. The conditions then become substantially equivalent to those in Method IA.

If the reagent is available in fine powder only or in a loosely textured condition, it should be fused if such a procedure is permissible, or a portion can be moistened with water and rapidly evaporated to dryness. From the crusts thus formed compact fragments may be selected.

Just as in Method I, better results may sometimes be obtained if the substance to be tested is added to the reagent; in this case the solid substance is added to the reagent drop. This procedure is limited to a few very special tests. The best example is that of the bismuth sulphate test for the alkali metals.

The addition of the reagent as a solid rather than in solution is also advantageous in reactions resulting in the precipitation of a compound in which the reagent does not enter into combination; as, for example, the precipitation of a compound by the introduction

of a like ion, or simply by increasing the concentration of salts in solution.

Typical Applications:

See Sodium, Method B, page 58.

Bismuth and Antimony, Method A, page 204.

Electropotential Series, page 373.

Method III: The reagent solution is drawn in a narrow channel across a dry film, obtained by evaporating to dryness a solution of the substance to be tested. — There are a few identity tests which give far better and more rapid results if performed in this manner than when the reagents are applied by Methods I or II.

Residues for reactions performed by Method III should consist of thin films in which the material to be tested is distributed uniformly over a circular area about 7 mm. in diameter. Such films are obtained by gentle evaporation. Place a drop of the material to be tested at the corner of a scrupulously clean slide; spread it out in a thin drop not less than 7 mm. in diameter. Warm the preparation and blow gently upon it to hasten evaporation to the saturation point. Reheat and again blow. Spread the drop to a film if necessary, and continue blowing on the heated preparation until the liquid has evaporated leaving a thin uniform perfectly dry film. Care must be observed that at no time shall the temperature be raised to the boiling point, and that the residue is not heated after it becomes dry. Unless these precautions are observed the residue will not adhere to the object slide, and when the reagent is drawn across, the dry material will be loosened and the whole area flooded.

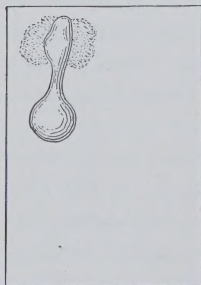


FIG. 22.

Tipping the object slide and heating nearer the center of the slide than the drop will prevent the liquid from creeping and spreading over too great an area.

In case a film is obtained surrounded by a ridge of solid material coarsely crystalline in character it is advisable to remove this ridge by means of a tiny spatula, using it shovel-wise.

Sufficient reagent is dissolved in a drop of water to produce an almost saturated or fully saturated solution. This drop should be placed about 3 mm. (not more) from the dry film and drawn across the dry film with a quick stroke of a glass rod or a platinum wire, care being taken

to avoid rubbing the glass in leading the reagent across. The preparation should have the appearance shown in Fig. 22, page 34.

The reagent should never spread over the entire film but should remain as a narrow streak of liquid across the film of dry material. Under these conditions the substance subjected to the reaction dissolves in a minimum of solution saturated with the reagent. If an element, salt, or compound is present, capable of forming a product of moderate insolubility, such a reaction product will separate almost at once, even if its solubility is not very low.

To insure the growth of crystals of suitable size for easy detection the slide should be slightly inclined after drawing the streak across, and held very slightly inclined for a few seconds before placing the object slide upon the stage of the microscope.

When the reagent flows over so as completely to cover the film of substance it is usually due to one or more of several causes: too thick a film; too large a glass rod; an object slide that is not clean; heating after the film has become dry and so detaching the crystals from the glass; too much reagent; the presence of excessively soluble or deliquescent compounds that do not remain dry or refuse to cling to the glass slide.

Typical Applications:

See Sodium, Method A, page 52.

Potassium, Method D, page 72.

Method IV: Upon failure to obtain a decisive test, owing to an insufficiently high concentration of the test drop, a separation of characteristic crystals can be obtained through the addition of another ion which will form a less soluble salt of the same nature.—Method IV is based upon the formation of a series of isomorphous compounds of decreasing solubilities. It is of value when the test drop is highly concentrated and evaporation will be followed by the separation of such a large amount of crystalline salts as possibly to mask the test for the ion sought. Time is saved and the apparent sensitivity of the reaction is increased.

An excellent example of this method is to be found in the testing for lead or for copper, by the triple nitrite method. Copper acetate or lead acetate and potassium nitrite are added to the acidified test drop. A triple nitrite of Pb^{++} , Cu^{++} and K^+ is formed, and separates in tiny black cubes if the concentration is above a certain minimum. Suppose that after the reagents have

been applied, no black cubes appear. A salt of cesium or of thallium can be added, for the cesium triple nitrite is less soluble than that of potassium and the thallium salt less soluble than that of cesium. The addition of Cs^+ or Tl^+ may therefore cause an immediate separation of the triple salt, and the sensitivity of the reaction in this particular concentration of Pb^{++} or Cu^{++} has been increased; but if we had allowed the original preparation to pass to dryness we probably would have detected neither Pb^{++} nor Cu^{++} , because the reaction would have been masked by the large amount of crystalline residue always present in this test.

Tests based upon Method IV are among the most interesting and instructive with which the analyst has to deal. To apply and interpret them intelligently, or to devise new tests based upon this principle, requires a good practical knowledge of the Periodic System.

Assuming that Method IA has been employed and that no reaction product has appeared, there is introduced (Method III) a solid fragment of a reagent forming a salt isomorphous with the reaction product first sought; by this addition the formation of a new and much less soluble phase has been facilitated.

Whenever there exists an isomorphous series of salts of decreasing solubility with increase or decrease of the atomic weight (or molecular weight) of the cation, one cation may be substituted for another, or two or more may be introduced into the same test drop.

Typical Applications:

See Potassium, Method A, page 68.

Lead, Method C, page 184.

Method V: The reagent is dissolved in alcohol and applied to the test drop or test film. — Alcoholic solutions of reagents or solutions of reagents in other liquids whose surface tensions are very different from that of water require a special technique, if satisfactory results are to be obtained.

If one attempts to apply a drop of an alcoholic solution to an aqueous drop, it is probable that reagent drop and test drop will flow all over the object slide, that the alcohol will forthwith disappear, and that there will remain a multitude of water droplets scattered here and there upon the surface of the object slide. Water and alcohol are perfectly miscible in all proportions, but

the physical reaction resulting from the mixing of two drops whose liquids have very different surface tensions prevents the general use of alcoholic solutions in microscopic qualitative analysis.

When an alcoholic reagent must be added to a test drop or when it is desired to add alcohol alone to a test drop, the aqueous solution should always be placed at the corner of the object slide. Tip the slide before applying the alcohol and just as the alcohol leaves the glass rod or pipette increase the inclination of the slide, and as far as possible allow the alcohol to flow upon the slide a very little at a time. Be ready to counteract the tendency of the alcohol to creep, by increasing the inclination of the slide to an almost vertical position.

Whenever possible, prepare a dry film of the material to be tested, and cause the alcoholic reagent to flow over the film. Hold the slide inclined a few seconds, in order that the reaction may have had time to take place.

Since alcohol has a tendency to flow over the edges of the slide, it is best to lay the slide upon a larger slide, with the corner occupied by the liquid projecting beyond the larger slide. This precaution is taken to prevent the mixture from flowing over the stage of the microscope.

If the non-aqueous liquid creeps to a marked degree a bit of "Plasticine" or paraffin can be placed upon a larger slide and the object slide held in an inclined position while being examined under the microscope. When this preventive measure is employed a low-power objective must be used and steps taken to induce the reaction product to acquire reasonably large dimensions.

Reactions involving the use of alcoholic reagents, or precipitations produced by the introduction of alcohol, can often be more conveniently performed in shallow watch-glasses, hollow slides or small glass evaporators.

Method VI: The reagent is incorporated into a natural or artificial fiber and the prepared fiber is dipped into the drop of solution to be tested.—The application of reagent-carrying fibers to microscopic analysis is due to Emich and Donau,³ who first showed that certain reactions could be obtained by using carriers of reagents, which were impracticable in microscopic analysis by ordinary procedures.

³ Emich: *Monats.* **22**, 670 (1901); **23**, 76 (1902); *Ann.* **351**, 426 (1907).
Donau: *Monats.* **25**, 545 (1904); *Ann.* **351**, 432 (1907).

One of the best examples is that of the valuable reagent H_2S . It was shown that a sulphide-carrying fiber laid in a drop could be made to indicate the presence or absence of the metals of the H_2S and $(\text{NH}_4)_2\text{S}$ groups, the fiber being used first in acid, then in alkaline solution. So, too, most of our indicators of acidity and alkalinity when incorporated in silk or viscose-rayon afford sensitive and conveniently applied tests.

In developing a fiber method, certain properties must be borne in mind.

1-The fiber must possess a strong adsorptive property for the reagent.

2-The concentration of the adsorbed chemical must be relatively high in the prepared fiber.

3-The fiber should hold the chemical if possible, and not "bleed" too readily when it is immersed in the test drop.

4-The fiber must not react with the adsorbed reagent so as to change its chemical nature even on long standing.

5-The prepared fiber must afford as sensitive a reaction as the free reagent itself.

With the above properties governing the prepared fibers, the following have been found satisfactory. Silk impregnated with red and blue litmus; silk with congo red; viscose-rayon with turmeric, potassium ferrocyanide or potassium thiocyanate; wool or guncotton with zinc sulphide; silk or viscose-rayon with gold.

Two methods of using the impregnated fibers in testing have been proposed:

A-A slender conical cylinder of wax is affixed to the slide adjacent to the drop to be tested. To the point of the cone one end of the fiber is attached by gently pressing it against the wax. The upper part of the cone is bent over at about 90° with its vertical axis, and the free end of the fiber thus made to dip into the test drop. The liquid rises part way up the fiber by capillarity and when examined under the microscope the fiber is partly acted upon and partly free.⁴

B-A small shallow test drop is used and the fiber so placed that half of it lies immersed within the test drop and half outside the drop.⁵ It is easy to follow the change in color, for

⁴ Emich: *loc. cit.*

⁵ Chamot and Cole: *Jour. Ind. Eng. Chem.* **9**, 969 (1917), **10**, 48 (1918).

both portions of the fiber can be seen in the same field of the microscope.

Typical Applications:

See Boron, Method A, page 156.

Zinc Sulphide Fibers, page 376.

Method VII: A compound is added which will color the reaction product, usually by adsorption or solid solution, and thus increase the sensitivity of the test because of the formation of a color image. — Examples of the principles involved in Method VII are to be found in the use of stains and dyes for the differentiation of cellular structures of animal or of vegetable origin; in the staining of $\text{Al}(\text{OH})_3$ with congo red and SiO_2 with malachite green; in the staining of fats with sudan red or alkanin or of fatty acids with nile blue; or the staining of starch with iodine.

Falling within the principle involved in Method VII is the coloring of alkali perchlorate crystals with permanganate and of those of silver sulphate with chromate.

No general directions are possible for tests performed under Method VII. Each individual test and reagent must be applied in accordance with the materials and the conditions involved.

Typical Applications:

See Manganese, Method c, 1, page 235.

Perchlorates, Method A, page 355.

Chromium, Method A, page 216.

Method VIII: Testing for the evolution of a gas by means of gels. — Gases generated within a gel or viscous liquid are held for a considerable time dispersed in the semi-solid medium in tiny bubbles.

The method serves as a means of ascertaining whether a substance dissolves with effervescence and gives off a gas under the influence of certain chemical reactions.

In general the method is not adapted to the identification of the gas given off, although in the case of some gases the gel may carry soluble compounds which will react with the gas set free in a reaction.

Dissolve in freshly boiled distilled water sufficient gelatin to make a gel that just "sets" on cooling. For a large drop of solution on an object slide one or two square millimeters of commercial sheet gelatin will be sufficient. It is essential that the

gel shall not possess too high a setting power, nor be so "thin" that considerable time and a low temperature are required for the gel to set.

The substance to be tested, if a solution, is evaporated to dryness in a thin film upon an object slide; if a solid, it is finely powdered and spread in a thin layer over a circular area about 5 mm. in diameter. Upon the dry material a drop of melted gel is dropped and caused to spread out in a thin layer extending a very little beyond the circumference of the film of substance. It may be necessary to warm the object slide to prevent too rapid setting. The preparation is then laid upon a cool surface until the gel has set.

The preparation is placed upon the stage of the microscope and focused. It is now ready for the application of the reagent that is to be used to test for the generation of a gas. A large drop of the reagent is placed close to the drop of jelly and brought into contact with it. As the reagent slowly diffuses into the gel it attacks the dry material. If a gas is set free tiny bubbles will appear throughout the gel as tiny black disks with a bright center. They are, of course, spherical in form, and behave as do air bubbles. (See *Vol. I*, page 368.)

If the gas is very soluble in water and is liberated too slowly bubbles will not remain visible for any appreciable time, but even under these conditions close observation will usually reveal their presence just as they are formed.

Other transparent gel-forming materials may be substituted for the gelatin, or substances with a high viscosity, even if they do not form gels, may be used to good advantage.

Having ascertained that a gas is given off it can be tested and possibly identified by employing the apparatus and procedure described in Method IX.

Typical Applications:

See Carbonates, page 296.

Method IX: Identification of a gas or vapor, by exposing a compound to the action of the gas or vapor. — A. The apparatus shown in Fig. 6, page 15, has been found convenient for the production of reactions between a gas or vapor and a reagent in solution.

The material from which the gas is to be evolved is placed in the

crucible, covered with a thin layer of freshly ignited asbestos fibers, and the reagent that is to cause the liberation of the gas is added. Before this is done a small object slide is prepared with a *very small* drop of the absorbing (or "fixing") compound. Immediately on the addition of the liberating agent, the object slide is inverted over the crucible, with the hanging drop at the center of the crucible opening. Crucible and cover are placed in the clamp so as to close tightly the apparatus and prevent the escape of gas. The crucible is then *gently* warmed to favor the decomposition of the material being tested and the diffusion of the gas so as to bring it in contact with the hanging drop. After a short interval, and before any appreciable amount of steam has condensed, the slide is removed, turned over, and the drop of liquid examined under the microscope either directly or after the addition of a suitable reagent. If a reagent is contained in the hanging drop, the formation of a precipitate may often be observed under the microscope without uncovering the crucible, thus increasing the sensitivity of the test.

When dealing with very small amounts of a readily diffusible gas or vapor, and when there is believed to be danger of loss, it may be wise to cover the crucible with the prepared slide before the liberating reagent is added, leaving a small opening through which the liberating reagent is added through a capillary pipette. The cover is slid over the opening the instant the reagent has been added.

This procedure is applicable to the detection of gases such as CO_2 , HCN , H_2S , etc., and vapors of Br_2 , etc. It is also of value in the oxidation of loosely bound sulphur by Br_2 vapors and in the chlorination or oxidation of compounds by Cl_2 .

B. If a fragment of a solid reagent is to be exposed to a gas the apparatus shown in Figs. 23, 24, and Fig. 25, page 42, can be used. The gas generated or liberated in the retort *G* passes over the reagent *S* in the capillary tube *T* and the progress of the reaction can be followed under the microscope.

When employing this apparatus there should always be a loose wad of absorbent cotton, glass wool, or asbestos at *C*, to prevent the mechanical carrying over of particles from the effervescing material, or droplets of water or liberating reagent. The capillary tube *T* is attached to the retort by means of a short piece of rubber tube *R*. The tubulation is closed by a wooden or rubber

plug *P*. The manipulation of the component parts of the apparatus will be obvious from the diagram.

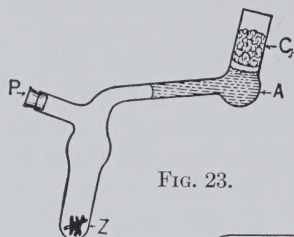


FIG. 23.

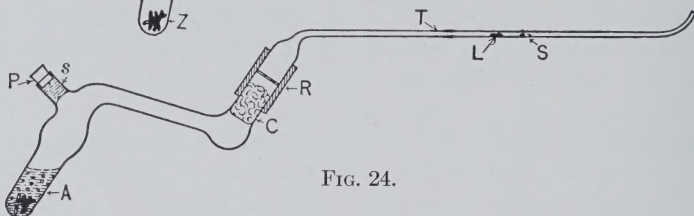


FIG. 24.

Apparatus for the Detection of an Evolved Gas.

For the observation of the reagent *S* the tube is held upon the stage of the microscope by means of the stage clips, the fragment *S* being moved to the center of the field. It is always best to lay *T* upon an object slide, and after clamping in place, a large drop of immersion oil is applied at *S*. This eliminates the heavily

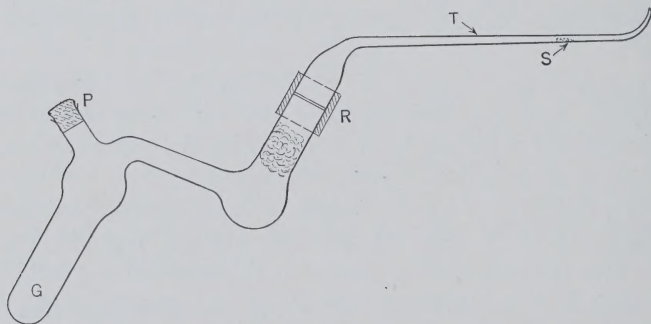


FIG. 25. Apparatus for the Detection of an Evolved Gas.

contoured refraction image of the tube and enables the worker more readily to follow changes in the reagent fragment.

When the gas evolved is heavier than air the drawn-out tip of the tube should be turned up as shown in the diagram, but if the gas is lighter than air the tip should be turned down.

When the tip is turned down a gas can be made to pass into a drop of reagent in which a reaction may be produced.

For further details see Detection of Arsenic, page 199.

Typical Applications:

See Ammonium, pages 75, 76.

Arsenic, Method A, page 199.

Bromides, Method B, page 343.

Method X: Testing with hydrofluoric acid, ammonium fluoride, or with fluosilicic acid. — Before undertaking any tests or performing reactions in which fluorine compounds are used as reagents in neutral or acid solutions, it is necessary to take steps to guard against injury to microscope and accessories by the corrosive action of any HF that may be set free. Unless these precautions are taken there is great danger of permanently damaging the objectives, the condensers and the polarizing prisms.

First, remove all objectives from the nosepiece save the one that is to be used; this will probably be the 32-mm. or the 16-mm. objective. Remove the substage condenser and the polarizer, and set all these accessories far to one side on the work table where they will be safe from attack by HF fumes.

Protect the objective by a shield such as is shown in Fig. 26. This consists of a brass cylinder fitting over the objective and made gas tight by a rubber ring. In the lower opening of the cell a No. 1 cover-glass is sealed in place with Canada balsam, shellac, or other resin. Before using the objective to view the preparation, examine the sealed-in window to make certain that the cement is free from holes or fissures.

If a protecting cell is not available place a large drop of immersion oil upon the bottom lens of the objective and press a small No. 1 cover-glass against the lens. The cover-glass will remain in place and the lens will be protected from HF fumes for the short periods required for an examination of the preparation. Oil is safer than glycerin for attaching the protecting cover-glass to the objective.

As a further precaution *work quickly*. Do not allow a prepara-

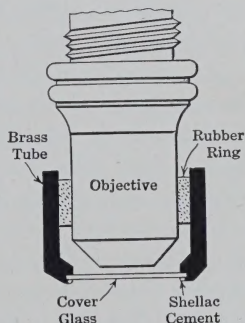


FIG. 26. Shield for the Protection of Objectives.

tion to remain more than a few seconds at a time on the stage under an objective. Use as low a power (long working distance) as is consistent with a satisfactory resolution of the crystals formed in the test drop.

If a number of preparations are to be studied, it is wise to remove the cover-glass from time to time, wipe off the oil and add a fresh drop of oil and a new cover-glass, for although HF is theoretically not soluble in oil it will be found that objectives are nevertheless attacked after long exposures and continued usage.

It is always good practice to relegate an old objective to work with HF, for if damaged the loss is negligible.

Reactions involving HF may not be performed on glass object slides, because they will be attacked and various fluosilicates will be formed. Platinum foil or lead foil cannot be used because they



FIG. 27. Capillary Tube for Sublimations. (Full size.)

are opaque. Glass stirring rods cannot be employed. Use a platinum wire.

An object slide may be protected by coating it with Canada balsam and baking it in an oven until the varnish has lost practically all its volatile components; when cool the slide should have a hard thin film, free from air bubbles and fissures. Always examine the surface under the microscope to be sure that no openings are present. Or the slide may be rendered safe by a coating of "Zapon," "Duco," or other cellulose base varnish. Or several thin coatings of a copal varnish may be applied. A coating of "Bakelite" or similar chemical plastic gives an excellent slide, but before such a slide is used it should be carefully scrutinized with a lens to make sure there are no fissures, for most of the synthetic varnishes, when spread on glass, develop on hardening a vast number of very tiny fissures.

Far better than coated slides are slips 35 mm. $\times$ 25 mm. cut from 1-mm. thick sheets of celluloid or of cellulose acetate. Since these materials are free from SiO_2 and alkali salts, reactions involving the use of HF or NH_4F can be performed without fear of contamination by these objectionable substances.

The chief objection to cellulose nitrate and cellulose acetate object slides is that it is difficult to find pieces that are not badly scratched or full of other defects. They are also quite easily softened by heat and the former are very flammable. If it is necessary to heat a preparation it is unwise to use a free flame; it is safer to heat a metal plate to the requisite temperature and lay the preparation upon it. (See Fig. 1, page 5.)

When it is necessary to heat, rather than warm a preparation, this should be done on platinum foil, and after cooling the material can be transferred to a transparent slide for examination under the microscope.

Method X can be used in the detection of the elements Si, Ti, Zr, Ge, Cb, Ta, Na, Ba, Li, Al.

Typical Applications:

See Sodium, Method C, page 63.

Hydrogen Ion Concentration. — The determination of hydrogen ion concentration, though properly belonging to the field of quantitative analysis, is frequently of use in microscopic work, even though only approximate values are obtained. Recognition of the presence of "strong" or "weak" acids or bases, or of their salts, is sometimes useful as confirmatory evidence in identity tests. The addition of a buffer salt such as ammonium acetate is common practice when the presence of strong acids interferes with the tests in question. The control of the acidity or alkalinity of solutions in which reactions are to be carried out deserves more emphasis than it usually receives in analytical work.

Very exact determinations upon small drops are perfectly practicable by electrometric methods using micro-electrodes which may be handled by a micro-manipulator and thus introduced into organs, tissues, cells, tiny droplets, etc.⁶

Colorimetric determinations by means of indicators are more convenient and are usually sufficiently accurate for most work. In order that colors may be compared under the microscope, a

⁶ Lehmann: *Biochem. Zeit.* **139**, 213 (1923).

Taylor: *Proc. Soc. Expt. Biol. Med.* **23**, 147-50 (1925).

Taylor and Whitaker: *Protoplasma* **3**, 1-6 (1927).

Keller: *Naturwiss.* **17**, 100-3 (1929).

Deidar: *Zeit. wiss. Mikros.* **46**, 361-8 (1929).

relatively intense color tint is necessary unless reflected light is employed and the preparation is viewed upon a pure white field, or unless preparations and standards are contained in capillary tube cells and observations are made with a comparison microscope or a comparison eyepiece. (See *Vol. I*, pages 37, 68, 189.) Test drops spread out upon a slide usually give too thin a layer of liquid to permit color differentiations by transmitted light. Drops standing up in tiny spheres upon an oiled slide yield an image too heavily contoured to be practicable, although such spherical drops can be employed by using reflected light and a white background.⁷

Fibers impregnated with the dyes used as indicators do not yield results that are readily interpreted, though they may serve in rough estimates of "acidity" or "alkalinity"; *e.g.*, litmus silk fibers as applied to solutions give a red or a blue as the case may be, but variations in hue due to slight changes in *pH* cannot be recognized on the colored fiber. Wholly aside from this, litmus may indicate, with certain substances, a neutrality at several quite different *pH* values.⁸

Since certain of the useful indicators are almost insoluble in water, the addition of a tiny fragment of the dye to the test drop is sometimes impracticable.

A solution of the dye in dilute alcohol is commonly used, and a tiny droplet is added to the test drop.⁹ If comparative estimates are to be made solutions of known *pH* to which the same concentration of indicator has been added are used for the comparisons.

Comparison of test drop with standards can be made by microcolorimeters; by projecting into the field by means of the Abbe condenser a series of uniformly illuminated standards;¹⁰ or by observing standards simultaneously with the field of view by means of a drawing camera. The image of one standard at a

⁷ Richards: *Science* **68**, 185 (1928).

⁸ Robinson: *Jour. Biol. Chem.* **53**, 445 (1922).

⁹ Indicators may be introduced into tissues or organs by pipettes handled by the micromanipulator. Schmidtman: *Zeit. wiss. Mikros.* **42**, 81 (1925); Peterfi; *ibid.* **45**, 56 (1928). The dye may be dissolved in collodion, which is evaporated to give a film, on which tiny droplets may be placed in a series and compared under the microscope. Wagner: *Biochem. Zeit.* **74**, 239 (1916).

¹⁰ Pantin: *Nature* **111**, 81 (1923).

Needham: *Proc. Roy. Soc.* **98B**, 259-86 (1925).

time is brought into the field in juxtaposition with the test drop. This is readily accomplished by tipping the mirror of the microscope or that of the camera or by moving the series of standards themselves.

To cover properly the range of pH values from 1 to 10 a series of overlapping indicators is necessary. A convenient series is as follows:

pH Range	Indicator	Acid Color	Alkaline Color
0.2 to 1.8	Acid cresol red	red	yellow
1.2 2.8	Meta cresol purple	red	yellow
2.6 4.2	LaMotte yellow	red	yellow
3.0 4.6	Bromophenol blue	yellow	blue
3.8 5.6	Bromocresol green	yellow	blue
5.2 6.8	Chlorophenol red	yellow	red
6.0 7.6	Bromothymol blue	yellow	blue
7.2 8.8	Cresol red	yellow	red
8.0 9.6	Thymol blue	yellow	blue
8.3 10.	Phenolphthalein	colorless	red

For qualitative indications it is only necessary to find which of the above indicators give an acid color and which an alkaline color. Since the pH value for "neutrality" is 7, it is usually best to start with bromothymol blue (6.0 to 7.6). If the test drop gives a blue color with this indicator the pH of the drop is 7.6 or greater, if yellow, the pH must be about 6 or less, if green the pH lies somewhere between 6 and 7.6, the numerical value depending upon whether a yellow green or a blue green hue is produced. According as the indication is blue or yellow, the next indicator overlapping higher or lower in the scale is chosen and the test made. This is continued until a point is found where one indicator gives an "acid" reaction and the next an "alkaline" reaction.

In this manner a fairly close estimate of the pH of the solution can be made without the necessity of employing standards and matching the color obtained with the final indicator used.

Most qualitative tests are made upon solutions containing dissolved salts which exert a sufficient buffer action to enable reliable estimates to be made. In the absence of salts in solution a suitable buffer must be added. Space forbids a discussion of this phase of the problem. For further information the reader is

referred to texts devoted to the determination of hydrogen ion concentration.¹¹

Determination of Molecular Weights. — Barger¹² has devised an ingenious method for determining the molecular weight of substances in various solvents. It depends on the fact that the vapor tension of a solvent is lowered in proportion to the molar concentration of the dissolved material (dissociation being neglected), and that of two solutions the one having the higher molar concentration will have the lower vapor tension.

The substance of unknown molecular weight, in a solution of known concentration, is drawn into a 1.5-mm. capillary tube, alternately with a solution of a reference substance in the same solvent and having known molar concentration. A series of drops each about 1 mm. long, and separated by small bubbles of air, is thus formed in the capillary tube, and on standing for several hours at room temperature, or for a much less time at elevated temperature, isothermal distillation of the solvent takes place, from the drops of lower molar concentration to those of higher molar concentration. The length of the drops is measured before and after the run, by means of an eyepiece micrometer, and a comparison of the molar concentrations is made. By preparing several series, using reference solutions of different molar concentrations, the molecular weight of the unknown may be ascertained with considerable accuracy. For details of the method, especially as applied to organic substances, and for a full discussion of its accuracy and possible errors, the reader is referred to the original publications of Barger and Yamakami.

¹¹ Clark, W. M. *The Determination of Hydrogen Ions*. 3rd ed. (Williams & Wilkins Co., Baltimore, 1928).

Michaelis: *Hydrogen Ion Concentration* (Williams & Wilkins Co., Baltimore, 1926).

A. P. H. A.: *Standard Methods* (A. P. H. A., New York).

LaMotte Chemical Products Co.: *The ABC of Hydrogen Ion Control* (Baltimore).

Bausch & Lomb Optical Co.: *Hydrogen Ion Colorimetry* (Rochester, N. Y.).

¹² Barger: *Jour. Chem. Soc.* **85**, 286 (1904); **87**, 1756 (1905).

Yamakami: *Biochem. Jour.* **14**, 103 (1920).

Rast: *Berichte* **54**, 1979 (1921).

Emich: *Praktikum* (1931) p. 123; *Lehrbuch* (1926) p. 112.

Friedrich: *Mikrochemie* **6**, 97 (1928).

Jasinski: *Roczniki Chem.* **9**, 623 (1929).

Pregl: *Die quantitative organische Mikroanalyse* (1930) p. 237.

Quantitative Estimations. — Numerous reliable microanalytical methods for both inorganic and organic material have been developed by Donau, Pregl, Emich and others.¹³ The manipulative procedures are essentially those of macroscopic quantitative analysis, carried out on a greatly reduced scale. Since they do not involve the use of the microscope, except incidentally, they are not included in the present work. However, many of the methods of handling small amounts of material which have been developed in connection with micro-quantitative analysis will be found highly valuable in connection with microscopical qualitative examinations.

The rough estimation of the relative amounts of the various ingredients present in a mixture is sometimes possible in qualitative testing; it is based on the amount of precipitate obtained, and, if known mixtures or known dilutions are employed, can be of approximate quantitative significance.

It is also possible to measure with considerable accuracy the volume of a solution of known concentration required to effect complete precipitation in a micro test; the "end point" may be observed microscopically. This serves as a basis for volumetric analyses.

The solution can be measured dropwise by means of a small loop of fine platinum wire or a very fine pipette, previously calibrated. Graduated capillary pipettes, such as are used for dilution in blood counting, are very convenient. Ordinary drawn-out glass tubing, calibrated by weighing filled with mercury, and graduated in aliquot parts, can also be used.

¹³ Donau: *Arbeitsmethoden der Mikrochemie* (1913).

Pregl: *Quantitative Organic Microanalysis* (Translated by Fyleman) (1930); *Die quantitative organische Mikroanalyse* (1930).

Emich: *Lehrbuch der Mikrochemie* (1926); *Methoden der Mikrochemie* (Abderhalden's *Handbuch der biologischen Arbeitsmethoden*, Lfg. 15); *Umsetzungen kleiner Stoffmengen (Mikrochemie)* (Stahler's *Handbuch der Arbeitsmethoden in der anorganischen Chemie*, Bd. 2, Hfte. 2); *Mikrochem. Praktikum* (1931):

CHAPTER III

THE DETECTION OF THE ELEMENTS OF GROUP I OF THE PERIODIC SYSTEM

Li; Na; K, (NH₄), Rb, Cs; Cu, Ag, Au

Group I in the Periodic Classification of the elements consists of the transitional element lithium; a main sub-group — the alkali metals — sodium, potassium, rubidium, cesium; and a secondary sub-group — copper, silver, gold.

From the point of view of microscopic qualitative analysis lithium is strictly a transitional element more closely related to Group II, for although its very soluble halogen salts resemble those of the alkalis, its normal carbonate and its phosphates, being difficultly soluble in water, link it with the alkaline earths (calcium, strontium, and barium), but on the other hand, since its oxalate and sulphate are readily soluble, it is excluded from the analytical group calcium, strontium, barium. Moreover, lithium fails to yield crystalline precipitates with the reagents employed for the detection of the alkalis; hence analytically it falls in a group by itself.

Because sodium forms, with the halogens, crystals of the cubic system, isomorphous with like salts of potassium, rubidium and cesium, sodium is to be regarded as a member of the alkali group, but, save for the halogen salts, most of the simple salts of sodium crystallize in systems different from those of potassium, rubidium and cesium and differ from the salts of these elements in relative solubility and in analytical behavior. We may therefore consider that sodium like lithium falls in a separate analytical group by itself.

To the potassium group of the alkalis, potassium, rubidium, and cesium, we must add the element thallium, since most thallic salts respond to the same reagents used for the detection of these elements. For the same reason we must consider the radical NH₄ as also a member of this group, since ammonium salts are very apt to be mistaken for potassium salts.

In the potassium group, when the metal is united to a simple anion the solubility of the salt usually rises with the atomic weight of the element, but when in double or complex salts this relation seldom holds, and may on the contrary be quite the reverse, as for example, the chloroplatinates, chlorostannates, etc.

When the alkali metals are united with complex ions, very stable salts usually result; so stable, in fact, that it is sometimes difficult to obtain satisfactory tests for the component elements. In many instances it is necessary to heat the compound to be tested until the complex is destroyed, then treat with HCl or HNO₃, or even aqua regia, and test the solution for the alkali metals.

The great majority of the double and triple salts with which the analyst comes in contact contain one or more alkali metals. The identification of these double, triple, or complex salts is most easily accomplished by observations of crystal habit and optical properties, after a chemical test has shown what cations and what anions are present.

The members of the secondary sub-group of Group I, copper, silver, gold, seldom enter into any scheme for the microscopic detection of members of the main or primary sub-group; hence the consideration of their analytical behaviors can be deferred until the discussion of the analytical groups into which each one properly falls. From their position in the periodic system, copper, silver, and gold are the links between Group I and Group VIII. It has therefore appeared to be more logical to treat these elements in connection with the discussion of the micro-analytical behavior of Group VIII; but in their lower valence, copper and gold (and thallium) are more closely affiliated with the other members of Group I than they are with the elements of Group VIII. These analogies are shown in the monovalent halogen compounds, in the isomorphism of CuCl and AgCl with NaCl, in the isomorphism of Ag₂SO₄ with anhydrous Na₂SO₄, and in the isomorphism of the "alums."

Although the halogen compounds of the elements of the secondary sub-group of Group I have formulas similar to those of the alkalis, they differ greatly from the alkalis in their properties. CuCl, AgCl and AuCl are white salts, insoluble in water, but soluble in concentrated HCl, in NH₄OH and in alkali thiosulphates.

DETECTION OF SODIUM

A—By means of Uranyl Acetate — $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$.

Compound Formed — $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ or

$\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x \text{H}_2\text{O}$.

The reagent — a very concentrated solution of uranyl acetate strongly acidified with acetic acid — is applied by Method III, page 34. The reagent drop should be large and highly concentrated.

The reaction product — sodium uranyl acetate — is a salt of high molecular weight, strong crystallizing power and low solubility in cold water. It is quite soluble in hot water and sufficiently stable (especially in the presence of free acetic acid) to permit recrystallization from hot water. This salt separates under the conditions of the test in the form of very faintly yellow regular tetrahedra or triangular plates of the cubic system. (Fig. 28, Fig. 30, page 53.) The crystals are therefore isotropic and can be easily differentiated from other uranyl salts which may separate, but which are anisotropic. The reagent separates in short stout orthorhombic prisms.

Viewed under the microscope by transmitted light the perfect tetrahedra of this double acetate of sodium and uranyl sometimes appear to be black, on account of internal total reflection.

If instead of uranyl acetate, zinc uranyl acetate — $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ — is used as the reagent, in addition to the double acetate of sodium and uranyl there is formed a triple acetate of sodium, zinc, and uranyl which separates in very characteristic monoclinic polysynthetic twins possessing an octahedral aspect; these crystals appear to be colorless, but are in reality faintly yellow. (Fig. 31, page 53.)

No element other than sodium yields crystals in any way resembling the double and triple acetates above described.

The reagent should be strongly acidified with acetic acid to prevent hydrolysis and to provide sufficient $(\text{C}_2\text{H}_3\text{O}_2)^-$ ions to insure the formation of the double and triple acetates which are to serve as the basis for the test.

Free mineral acids must be absent or not more than a trace be present.

Ions uniting with uranium to form compounds insoluble in water or in dilute acetic acid may prevent the formation of the sodium double salt by removing the UO_2 ions. Those most frequently met



FIG. 28. Sodium with Uranyl Acetate. 60 $\times$:

FIG. 29. Potassium with Uranyl Acetate. 60 $\times$.

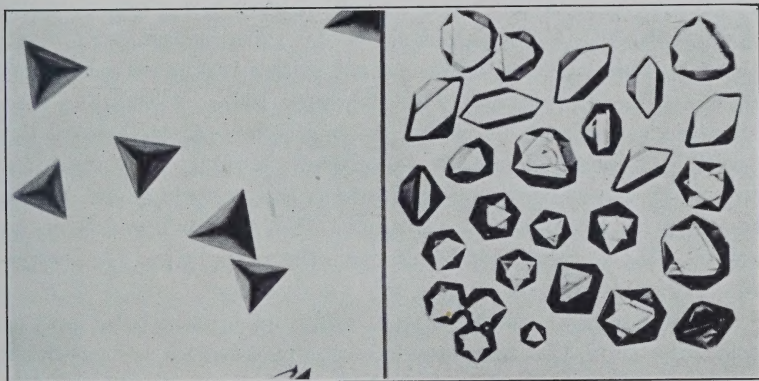


FIG. 30. Sodium with Uranyl Acetate. 300 $\times$

FIG. 31. Sodium with Zinc-Uranyl Acetate. 100 $\times$

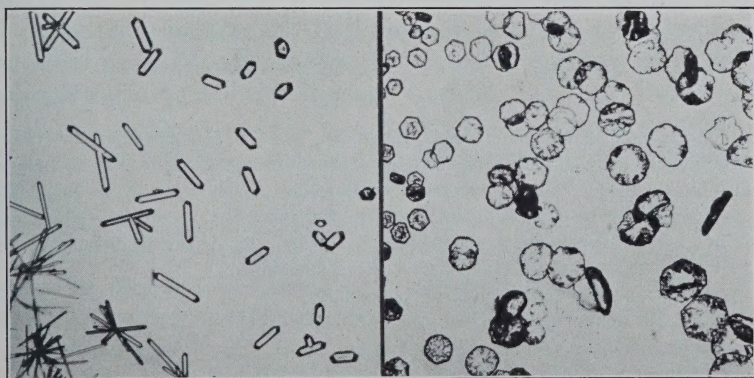


FIG. 32. Sodium with Bismuth Sulphate. 100 $\times$.

FIG. 33. Potassium with Bismuth Sulphate. 100 $\times$.

with are CO_3^{--} , HCO_3^- , OH^- , PO_4^{---} , $\text{Fe}(\text{CN})_6^{----}$. In such an event the amount of uranyl acetate employed must be in excess of that required to unite with all of the precipitating ions present. To accomplish this completely, flood the dry film; after a few seconds decant or filter, transfer the clear solution to a clean slide and allow to evaporate to crystallization; crush some of the crystals first formed so as to prevent the formation of a metastable solution.

When the solution of the reagent is being drawn across the dry film of the material to be tested, care should be taken to avoid flooding the entire film. If flooding does occur it is usually best to prepare a new film and test anew.

Potassium, rubidium, cesium, thallium (Tl^+), ammonium, and silver also form double uranyl acetates having the type formula $M(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$. But these salts separate in long slender needles or slender tetragonal prisms terminating in pyramids. (Fig. 29, page 53; Fig. 100, page 169.) These salts constitute an isomorphous series, as might be expected from the position of these elements in the periodic system; they are more soluble than the corresponding sodium salt and therefore do not separate so readily from solution. The ammonium salt is so soluble that it rarely separates until the preparation has evaporated substantially to dryness.¹

Because sodium uranyl acetate differs in crystal habit and in solubility from the corresponding double acetates of the other alkali metals it is possible to detect sodium and potassium (Rb , Cs , Tl^+) simultaneously, providing potassium is not in too great excess. The sodium salt separates first, then as the test drop passes to dryness the potassium group salts appear. When the proportion of $\text{Na}^+ : \text{K}^+$ reaches 1 : 3 the reaction for sodium is very poor and uncertain and may completely fail when the ratio is 1 : 5 or greater.² These same ratios hold approximately for

¹ Lenz and Schoorl: *Zeit. anal. Chem.* **50**, 263 (1911), suggested the use of $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ as a reagent for sodium in place of $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$, because of the much greater solubility of the ammonium salt. Its crystal habit is also in its favor, but the sensitivity of the reaction for sodium is not increased and its use precludes the possibility of the simultaneous detection of other alkali metals when testing for sodium.

² Schoorl: *Zeit. anal. Chem.* **48**, 604 (1909).

Lenz and Schoorl: *Zeit. anal. Chem.* **50**, 263 (1911).

Behrens-Kley: *Mikrochemische Analyse*, p. 32.

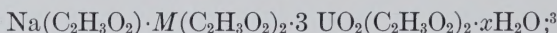
Chamot and Bedient: *Mikrochemie* **6**, 13 (1928).

rubidium, cesium, and thallium. If, therefore, these elements are present in larger amounts than sodium they must first be removed through the addition of perchloric acid or tartaric acid. The sodium salts of these two acids are so much more soluble that it is easy to decant the sodium-containing mother liquor from the precipitated perchlorates or tartrates. The decanted mother liquor is evaporated to dryness and tested as directed, or better still use zinc uranyl acetate as reagent.

Acetates of calcium, strontium, and lead, when tested as described, yield masses of colorless, fine hair-like crystals (trichites) or exceedingly fine needles in clumps or bundles; occasionally long slender prisms may be formed. The bundles of needles appear brown by transmitted light. Barium acetate at first yields fine needles, but in a very short time large square plates appear which have a very characteristic appearance; finally, as the preparation goes to dryness, clusters and sheaves of relatively stout prisms are formed. The square plates appear to be constant and peculiar to barium. The composition of these interesting double(?) acetates of the alkaline earths is at present unknown; they are not readily formed from the mineral acid salts of these elements.

When calcium, strontium, barium, lead, or lithium are present in larger amount than sodium, the sensitivity of the sodium reaction is greatly reduced or the reaction for sodium may be completely inhibited. Boron may act toward sodium in a similar manner (Behrens). Sodium appears to be sometimes combined with these interfering elements in a complex which uranyl acetate is not powerful enough to destroy. Several evaporations to dryness with strong HCl will usually destroy the complex and permit the recognition of sodium. Sometimes a gentle ignition before the treatment with HCl will improve the character of the test; or even better, dilute H_2SO_4 can be added, care being used to avoid any marked excess. The supernatant liquid is decanted from the precipitated sulphates, evaporated to dryness and any excess of H_2SO_4 is fumed off. The test for sodium is then made on the residue as usual. Lithium is, of course, not removed by this treatment, but can be precipitated as carbonate or phosphate, using the ammonium salts; but if either of these procedures is followed, it must be remembered that the residual carbonates must be destroyed with acetic acid and that PO_4^{--} ions precipitate UO_2^{++} .

When, in addition to sodium, certain bivalent ions are present, there will be formed, not isotropic tetrahedra, but weakly refractive anisotropic pseudo-octahedra and bipyramids which are monoclinic polysynthetic twins, (Fig. 31, page 53); members of an exceedingly interesting isomorphous series of salts having the general formula



in which

M may be Cu^{++} , Mg^{++} , Zn^{++} , Cd^{++} , Mn^{++} , Co^{++} , Ni^{++} , Fe^{++} .⁴

These triple acetates vary in their solubilities and hence yield crystals varying in size in the test, but all have the same habit. As stated above, several of these triple acetates are known to exist as metastable compounds at temperatures above that of the room, hence the test should not be made upon a warm slide; all of them are prone to form metastable solutions, therefore before deciding that a test is negative, crush some of the material crystallizing at the edges of the reagent channel, and draw the fragments into the mother liquor.

All attempts thus far have failed to produce a triple uranyl acetate of the type formula given above in which the Na^+ is replaced by K^+ , Rb^+ , Cs^+ , Li^+ , Tl^+ , Cu^+ , Ag^+ , or Au^+ .

Since the sodium content called for by theory in these triple acetates is less than 2 per cent, one would expect that the sensitivity of this reaction for sodium would be considerably greater than that afforded by the double acetate. In practice, however, we find that there is little difference, the limiting value in each case being about 0.1μ gm. of sodium, when dealing with simple mixtures, while in the case of very complex mixtures or complex ions the sensitivity may fall to 0.5μ gm. The presence of the other

³ The water of crystallization is usually given as $9 \text{H}_2\text{O}$ but recent investigations have shown that the water of crystallization varies with temperature and that the salt crystallizing out usually has an indefinite amount of water of crystallization. See Miholic: *Bul. Acad. Sci. Zagreb Univ.* **1920**, 16.

Chamot and Bedient: *Mikrochemie* **6**, 13 (1928).

⁴ Cagpioti: *Rend. accad. sci. (3a)* **33**, 177 (1927) states that he has obtained $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 9 \text{H}_2\text{O}$ in rhombohedral uniaxial crystals, but neither Miholic nor Bedient were able to obtain a triple acetate with Na and Be when using spectroscopically pure Be unless the solution goes to dryness.

alkali metals or of the alkaline earths does not inhibit the triple acetate reaction for sodium.

Taking advantage of this fact, we may use the zinc salt $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ as a reagent for sodium, proceeding in the same manner as with $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$. The zinc salt is employed rather than that of one of the other members of the isomorphous series since zinc can be obtained free from sodium. We have been unable to purchase samples of the other triple-acetate-forming bivalent elements, such as Mg, Cd, Co, sufficiently free from sodium to permit their double uranyl acetates being used as reagents.

When the zinc double salt is employed as a reagent for the detection of sodium it is unnecessary first to remove the other alkalis or the alkaline earths.

It is obvious that $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ is a reagent of wider application than the mere detection of sodium. When applying this reagent the analyst may be guided by the following phenomena:

A—Isotropic tetrahedra separate — Na^+ present.

B—Isotropic tetrahedra followed by tetragonal prisms — Na^+ ; and K^+ , or Rb^+ , Cs^+ , Tl^+ , $(\text{NH}_4)^+$.

C—Tetragonal prisms or needles only — Na^+ may be present but other alkalis or alkaline earths interfere with Na^+ test. Test with ZnUO_2 acetate.

D—Trichites or bundles or masses of very fine needles — Ca^{++} , Sr^{++} , Ba^{++} , Pb^{++} ; (K^+ , Rb^+ , Cs^+ , Tl^+).

E—Monoclinic polysynthetic twins (pseudo-octahedra) — Na^+ present *and* one or more of the following: Cu^{++} , Mg^{++} , Zn^{++} , Cd^{++} , Mn^{++} , Co^{++} , Ni^{++} , Fe^{++} .

F—Square plates and masses of square plates — $\text{Ba}^{++}(\text{Sr}^{++}?)$.
G—Thin elongated plates with six sides and an acute angle of $90^\circ = \text{AgC}_2\text{H}_3\text{O}_2$; acute angle $49^\circ\text{--}50^\circ = \text{AgC}_2\text{H}_3\text{O}_2 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{Ag}^+$. Both these compounds have parallel extinction.

H—A heavy, more or less gelatinous, precipitate is produced. See page 54.

If the test drop is allowed to evaporate to dryness, spontaneously, there may appear *double* uranyl acetates of Li^+ , Cu^+ , Cu^{++} , Be^{++} ; and if Na^+ is absent, orthorhombic double uranyl acetates of

Ba^{++} , Mg^{++} , Zn^{++} , Cd^{++} , Pb^{++} , Mn^{++} , Cu^{++} , Co^{++} , Ni^{++} , Fe^{++} . All of these double acetates are too soluble to be useful as identity tests and moreover they lack sufficiently characteristic habits.

When testing for the presence of mere traces of sodium, glass object slides should not be used; recourse should be had to object slides of quartz or fused silica or celluloid. Concentrations or evaporations to remove mineral acids must be performed on platinum foil or silica slides.

Because of its affinity for sodium, uranyl acetate cannot be kept in glass vials where the salt will come in contact with the glass. Ebonite tubes or vials coated with ceresin wax or with a varnish may be used, or the reagent may be kept in paper rolls placed in a vial.

Always make a "blank" test on distilled water, acids, and all reagents, before deciding that traces of sodium are present in the material under examination.

Sodium-free uranyl acetate can seldom be purchased. Always extract the purchased uranyl acetate with 95 per cent alcohol, in which the sodium uranyl acetate is insoluble, using a platinum or silica container, crystallize the alcoholic extract in platinum or silica — use no glass.

Experiments. Test for sodium in:

- (a) — NaCl , HNa_2PO_4 .
- (b) — $\text{NaKC}_4\text{H}_4\text{O}_6$; and in $3(\text{Na}_2\text{C}_2\text{O}_4) \cdot \text{Fe}_2(\text{C}_2\text{O}_4)_3$.
- (c) — A mixture of NaCl and MgCl_2 .
- (d) — A mixture of Na_2SO_4 and ZnSO_4 .
- (e) — A mixture of NaCl and CoCl_2 .
- (f) — Test for K in KCl .
- (g) — Test for Tl in TlNO_3 .

B—By Means of Bismuth Sulphate — $\text{Bi}_2(\text{SO}_4)_3$.

Compound Formed — $3 \text{Na}_2\text{SO}_4 \cdot 2 \text{Bi}_2(\text{SO}_4)_3$.

The best results appear to be obtained when the test is performed according to Method II, page 32.

Prepare the bismuth sulphate as follows. Place two drops of concentrated H_2SO_4 upon an object slide, add one drop of water, add $\text{Bi}_2(\text{SO}_4)_3$ a little at a time with constant stirring and warming very gently until the solution appears to be almost saturated. Now add the least possible amount of dilute HNO_3 required to make a clear solution.

Moisten with concentrated H_2SO_4 a portion of the material to be tested, to convert to a sulphate. Heat so as to produce a stiff paste.

To the reagent drop add a small quantity of the pasty material to be tested. Warm gently. If sodium is present there should appear slender rods or short prisms with rounded or angular ends, singly or in crosses or X's, or in more or less star-like clusters. (Fig. 32, page 53.) The short, stout prisms are the most characteristic of the forms separating. Since characteristic crystals are formed only in warm solutions, it is essential to warm the preparation for a considerable time, for the crystals are usually slow in forming. Failure to detect sodium when this element is present in small amount often results from heating the preparation for too short a time.

The reagent drop must be perfectly clear and not so concentrated that when warmed sheaves and bundles of very fine needles appear. These needles are due to the separation of a bismuth sulphate of variable and uncertain composition. Not infrequently the acicular crystals develop into long thin colorless lath-shaped crystals, singly, or in irregular crosses, sheaves and radiating masses, but in a very short time the crystals disintegrate, dissolve, and are replaced by a second bismuth sulphate with a very different crystal habit, in the form of long, very slender, colorless needles, and hair-like crystals in large radiating clusters, sheaves and fan-like masses. By transmitted light these aggregates of acicular crystals appear to be brown in color (structural color). It is probable that they are the result of the separation of an acid bismuth sulphate of unknown composition.⁵

Since the metastable bismuth sulphate which first separates forms crystals which may closely resemble the sodium-bismuth salt, it is a wise precaution, when in doubt, to divide the large reagent drop into two portions; to one of these add the material to be tested for sodium; the other portion is used as a "blank"; both are subjected to the same heat treatment and the drops

⁵ Mayrhofer: *Mikrochemie d. Arzneimittel und Gifte*, states that, on heating, a basic bismuth sulphate separates, but it is difficult to understand how such a salt can separate in the reagent as prepared above, *i.e.*, in the presence of an excess of H_2SO_4 to which HNO_3 has been added. Moreover the salt in question does not comport itself like any of the basic bismuth sulphates which have been described. See Heinz: *Pogg. Ann.* **63**, 1844.

compared under the microscope. If the reagent drop has been properly prepared and not too strongly heated no crystals should appear.

The salt $3 \text{Na}_2\text{SO}_4 \cdot 2 \text{Bi}_2(\text{SO}_4)_3$ formed when sodium is present, may sometimes separate at room temperature, but this is unusual. Gentle heating of the preparation appears to be essential.⁶ The characteristic crystals are small, stout, colorless prisms, rarely terminating in well-defined angles. They group themselves in a characteristic manner. Between crossed nicols they exhibit parallel extinction.

This reaction is peculiar to sodium and to bismuth; no other elements or compounds form similar crystals in strong H_2SO_4 .

Potassium, rubidium, cesium and ammonium form with the reagent double sulphates having the general formula $3 \text{M}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$. These four salts are isomorphous. They differ from the sodium double salt not only in habit but also in composition. The crystals first appear near the edges of the reagent drop or scattered through it, in the form of thin round disks (Fig. 33, page 53); disks with serrated circumferences; symmetrical rosettes (of the same appearance as in Fig. 36, page 61); skeletons of hexagons or as perfect hexagons (Fig. 34, page 61; Fig. 118, page 209). The rubidium and cesium salts seem to form thicker hexagons than do potassium and ammonium.

Since the potassium group double bismuth sulphates are more soluble than the sodium bismuth sulphate, the detection of both sodium and potassium in the same reagent drop is possible; the characteristic crystals of the sodium salt are the first to appear in the immediate neighborhood of where the fragment of the material being tested was introduced; later the potassium (or rubidium, cesium, ammonium) salt appears nearer the circumference of the drop. Even a very great excess of potassium does not interfere with the test for sodium. In dealing with such mixtures it is sometimes advantageous to retard the separation of crystals by introducing into the reagent drop a very minute quantity of glycerin.⁷

Having satisfied oneself as to the presence or absence of sodium after several repeated gentle heatings of the preparation and examinations, it is wise to heat the preparation sufficiently to cause

⁶ See Behrens: *Anleit. mikrochem. Anal.* (1895), p. 34.

⁷ Behrens-Kley: *op. cit.*, p. 34.

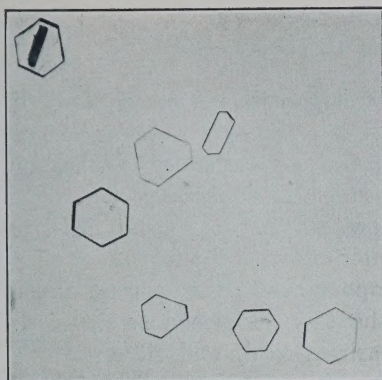


FIG. 34. Potassium with Bismuth Sulphate. 100 $\times$.

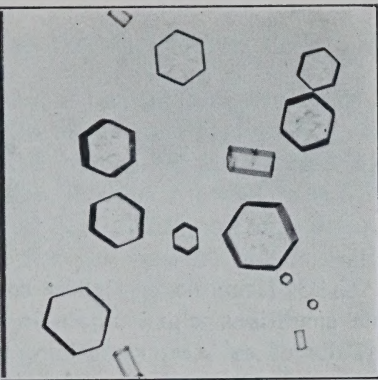


FIG. 35. Sodium with Ammonium Fluosilicate. 200 $\times$.

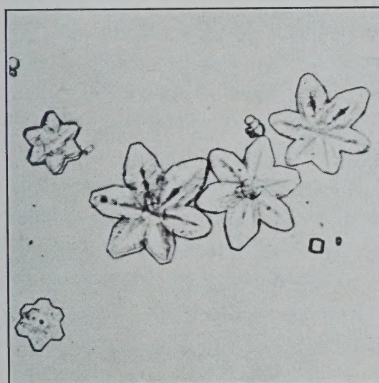


FIG. 36. Sodium with Ammonium Fluosilicate. 200 $\times$.

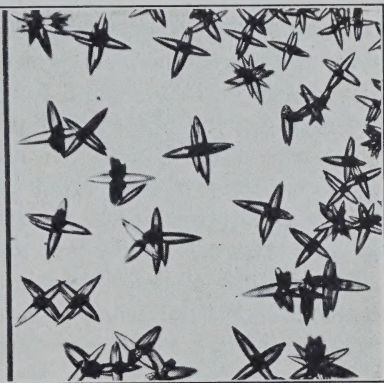


FIG. 37. Sodium with Potassium Pyroantimonate. 100 $\times$:

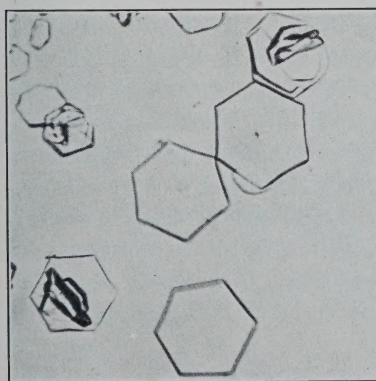


FIG. 38. Magnesium with Potassium Pyroantimonate. 100 $\times$.

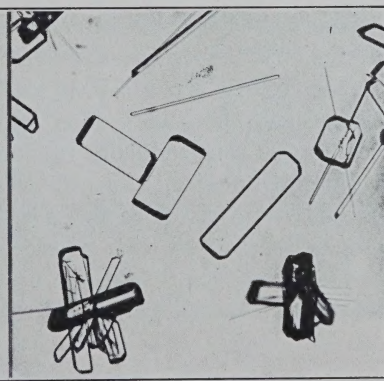


FIG. 39. Potassium with Tartaric Acid. 100 $\times$:

a slight evaporation, and search the preparation for crystals of the potassium group double sulphates. Since we are no longer concerned with the sodium salt, the separation of needles or prisms of bismuth sulphate will cause no confusion.

Although free HNO_3 may be present in the reagent, HCl is objectionable and may seriously interfere with the test.

Li_2SO_4 forms no crystalline compound with the reagent under the conditions which obtain in the test performed as directed.

Salts of calcium, strontium, barium, lead, and silver, which form difficultly soluble sulphates, may completely inhibit the test or may seriously affect its delicacy. The sulphates of all these elements are somewhat more soluble in concentrated H_2SO_4 than in pure water and from such solutions crystals may appear in forms somewhat resembling the sodium double sulphate. To guard against the possibility of error due to the presence of the above-mentioned elements it is best to remove them in part, before applying the test for sodium; this can be done by precipitating with dilute H_2SO_4 . An excess of H_2SO_4 must be avoided. The preparation is evaporated to dryness with gentle heat; the residue is extracted with a minimum quantity of water. The aqueous extract is evaporated to dryness and tested for sodium.

The bismuth sulphate test is more valuable for the detection of members of the potassium group than for sodium and is one of the best "micro" tests for bismuth since antimony gives no analogous reaction.

If no normal bismuth sulphate is available the reagent can be prepared from basic bismuth nitrate (bismuth subnitrate) as follows. Place a tiny drop of concentrated H_2SO_4 upon an object slide, add the basic bismuth nitrate a little at a time, with constant stirring, until no more dissolves; stir very thoroughly, for the solution of the basic salt is slow. Usually when saturation is reached and the basic salt is converted into a complex acid salt the drop of acid suddenly becomes white, solid, and swells to a considerable degree. Add water *slowly and in very tiny amounts*, stirring after each addition. The white salt should dissolve almost completely, giving a clear colorless solution, or at the most, merely an opalescent one. Add one or two drops of HNO_3 (1 : 4). To the reagent thus prepared add the material to be tested.

Experiments. Test for sodium in:

- (a) — NaCl.
- (b) — HNa_2PO_4 .
- (c) — A mixture of salts of Na and K.
- (d) — A mixture of salts of Na and Cs.
- (e) — A mixture of salts of Na and Ca.

C—By Means of Ammonium Fluosilicate — $(\text{NH}_4)_2\text{SiF}_6$.

Compound Formed — Na_2SiF_6 .

Apply the reagent by Method II (X), page 32, observing all the precautions given on page 43.

Before proceeding with the test always make certain that all the necessary precautions have been taken to guard against damage to the optical parts of the microscope.

Use a celluloid, cellulose acetate, or varnished object slide. If the last, examine it under the microscope to be sure the varnish film is intact and free from holes or fissures.

Use a platinum or nickel wire for handling reagents, stirring, etc.

After adding the material to be tested to the reagent drop, warm the preparation by laying it upon a warm metal surface. Celluloid is very flammable and great care must be observed if it is heated directly over the micro-flame.

Na_2SiF_6 crystallizes in rosettes (Fig. 36, page 61), six-sided plates (Fig. 35, page 61), and six-sided prisms with square or irregular ends or terminating in pyramids, belonging to the hexagonal system. The plates and rosettes (skeletons of hexagons) appear isotropic, the prisms exhibit *feeble* parallel extinction.

Under the microscope by transmitted light the crystals of Na_2SiF_6 appear to have a distinct pink color (Christiansen effect). Since the indices of refraction of this salt ($\omega = 1.313$, $\epsilon = 1.310$)⁸ are low and are close to that of water (1.333) great care must be exercised in properly adjusting the illumination of the preparation; otherwise the presence of the crystals in the test drop may be overlooked. To guard against this source of error Kley⁹ suggests allowing the preparation to evaporate to dryness at room temperature and covering the dry crystals with a liquid (benzene) having a higher index of refraction. (Monochlorbenzene, $n = 1.52$; or monobrombenzene, $n = 1.56$, give somewhat better results.)

⁸ Raiteri: *Atti*, V, **31**, I, 112 (1922).

⁹ Behrens-Kley: *Mikrochemische Analyse*, p. 34.

Allowing the preparation to pass to dryness and examining the dry residue is also useful.

Lithium forms a fluoride LiF of lower solubility than the fluorides of the alkalis and may appear in the test drop as colorless, isotropic cubes and octahedra.

When members of the potassium group are present in a ratio of 20 parts to 1 of sodium this test fails.¹⁰

In the presence of much calcium the hexagonal plates and short stout prisms are replaced by much longer and more slender prisms.

The fluosilicates of Mg^{++} , Fe^{++} , Mn^{++} , Cu^{++} , Ni^{++} , Co^{++} , Zn^{++} , Cd^{++} , Hg^{++} corresponding to the formula $\text{MSiF}_6 \cdot 6 \text{H}_2\text{O}$ also crystallize in the hexagonal system (hemihedral forms) but their habits are all very different from that of the sodium salt; they are also much more soluble and are, therefore, not likely to be confused with the sodium salt.

Potassium, rubidium, and cesium form salts having the formula M_2SiF_6 , which crystallize only from very concentrated solutions in the form of tiny colorless cubes, octahedra, dodecahedra, and combinations of these forms. These salts are isomorphous and belong to the cubic system.¹¹ There is no danger of mistaking a member of the potassium group for sodium; even when cubes in suspension are viewed with diagonals in line with the axis of the microscope and appear to have a hexagonal outline, careful illumination and focusing should dispel the illusion that these crystals are hexagonal plates. Hexagonal crystals may sometimes be formed.

The lithium salt $\text{Li}_2\text{SiF}_6 \cdot 2 \text{H}_2\text{O}$ separates in monoclinic plates and prisms just as the preparation goes to dryness.

The salt $\text{Ag}_2\text{SiF}_6 \cdot 4 \text{H}_2\text{O}$ is tetragonal but is too soluble to be useful as an indication of the presence of Ag^+ .

Calcium, strontium and barium unite with SiF_6^{--} to form an isomorphous series of monoclinic salts of the formula $\text{MSiF}_6 \cdot 2 \text{H}_2\text{O}$, crystallizing in curious fusiform bodies, singly, in crosses, radiating masses, and irregular bristling clumps. The calcium and strontium salts are far too soluble to separate, save when the preparation has evaporated completely to dryness, but the barium salt is sufficiently low in solubility to reveal the presence of barium as well as sodium in the same test drop.

¹⁰ Schoorl: *op. cit.*, p. 141.

¹¹ K_2SiF_6 is usually cubic, rarely hexagonal, and is even more difficult to perceive than the Na^+ salt, for its index of refraction is 1.340 (Raiteri).

Because of its high solubility $\text{MgSiF}_6 \cdot 6 \text{H}_2\text{O}$ is not precipitated and only appears as the preparation goes to dryness, in the form of rhombohedra with strong birefringence. Mn^{++} and Fe^{++} are said to form salts isomorphous with the Mg^{++} salt. The crystal system of the zinc and cadmium salts has not been determined.

In the absence of $(\text{NH}_4)_2\text{SiF}_6$, a test for the presence of sodium (or barium) can be made by adding a little SiO_2 to the test drop, following this by the addition of NH_4F or HF and finally acidifying with HCl (or if barium is absent acidifying with H_2SO_4). The preparation is gently warmed and set aside for a few minutes in order to give time for the crystallization of Na_2SiF_6 .

These reactions are especially valuable in the analysis of silicates.¹² The finely powdered material is treated with HF or NH_4F , acidified, and the preparation treated as above described. But it must be borne in mind that other elements may appear in the place of silicon. If we write the general formula for this great group of fluosalts as $M^{++}(\text{RF}_6)^{--}$ or $M^{++}(\text{RF}_6)^{--} \cdot x\text{H}_2\text{O}$, M may be almost any element functioning as a cation and R may be silicon, titanium, germanium, zirconium, or tin. (See Fig. 93, page 137; Figs. 94, 95, 96, 97, page 159.)

In the case of the acid H_2SnF_6 a large number of salts have been made and described; some of these salts are polymorphic. Those which may separate upon the object slide in the course of a qualitative analysis are $\text{Li}_2\text{SnF}_6 \cdot 2 \text{H}_2\text{O}$; $\text{K}_2\text{SnF}_6 \cdot \text{H}_2\text{O}(\alpha)$; $\text{CaSnF}_6 \cdot 2 \text{H}_2\text{O}$; $\text{SrSnF}_6 \cdot 2 \text{H}_2\text{O}$; $\text{BaSnF}_6 \cdot 2 \text{H}_2\text{O}$ and $\text{CuSnF}_6 \cdot 4 \text{H}_2\text{O}$.

Fluosilicates of many organic compounds crystallize readily, and may separate in the course of a qualitative analysis.

Experiments.

- (a) — Test, as directed above, salts of Na in both neutral and acid solutions.
- (b) — In order to better appreciate the reason for employing celluloid slips, place a drop of water on a glass slide, acidulate (but add no Na), then add the reagents and examine the preparation.
- (c) — Try to obtain crystals of K_2SiF_6 from KCl .
- (d) — Add a little CaCl_2 to a solution containing Na and test as above.
- (e) — To a solution of NaCl add a little SiO_2 or a trace of sodium silicate, then add NH_4F and an acid.

¹² This system of silicate analysis was proposed over 50 years ago by E. Bořický and described in a monograph entitled "*Elemente einer neuen chemisch-mikroskopischen Mineral- und Gestein-Analyse*" (Prag, 1877). It may justly be regarded as the first attempt at systematic microscopic qualitative analysis.

(f) — Repeat using some Ti compound in place of that of Si. Then try in turn a compound of B; a compound of Zr; a compound of Ge.

(g) — Test a salt of Ba as above, then a mixture of Ba and Na. Note that it constitutes an excellent test for Ba even in the presence of Na.

(h) — Add to a solution of $\text{Al}_2(\text{SO}_4)_3$ a large fragment of NH_4F .

(i) — Test a Li salt with NH_4F .

DETECTION OF POTASSIUM

A—By Means of Chloroplatinic Acid — H_2PtCl_6 .

Compound Formed — K_2PtCl_6 .

Apply the reagent by Method I, page 30.

When a concentrated solution of H_2PtCl_6 is caused to flow into a dilute solution of a salt of potassium, acidified with HCl, there separate at once well-formed, brilliant, highly refractive ($n = 1.827$),¹³ deep-yellow octahedra (Fig. 41, page 67), and combinations of octahedron and cube. Elongated and distorted forms are also formed, and in shallow drops the octahedra, not being able to grow up or down, grow laterally and assume the form of "flattened" octahedra whose relation to an octahedron is puzzling to the beginner. The elongated octahedra resemble orthorhombic crystals, but an examination between crossed nicols will show that they belong to the cubic system.

Not infrequently preparations are obtained in which twinning is very marked. Threelings and fourlings are also formed. In the case of twins one type predominates; it results from the union in reversed position of the two halves of an octahedron where the dividing plane is parallel to the diagonally-opposite faces of the octahedron.

The best formed crystals and most satisfactory tests are to be obtained when the potassium ion is present in a chloride and the test drop contains a little free HCl, but much free HCl is to be avoided. HNO_3 or H_2SO_4 do not inhibit the reaction but reduces its sensitivity, hence the analyst may be led astray in his estimate of the relative amount of potassium present. It is always best to remove free mineral acids by evaporating to dryness and "fuming off."

Since the salt K_2PtCl_6 is only very slightly soluble in water (insoluble in alcohol) it is essential that the solution to be tested be quite dilute with respect to K^+ ions, otherwise skeleton crystals,

¹³ Raiteri: *Atti Accad. Lincei*, V, **31**, I, 112 (1922).

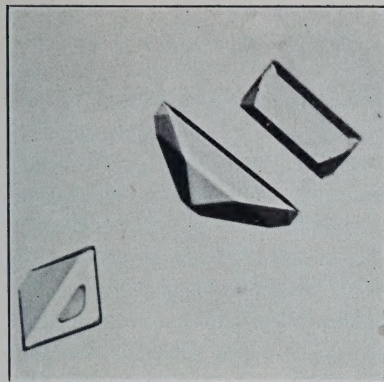


FIG. 40. Potassium with Perchloric Acid. 100 $\times$.

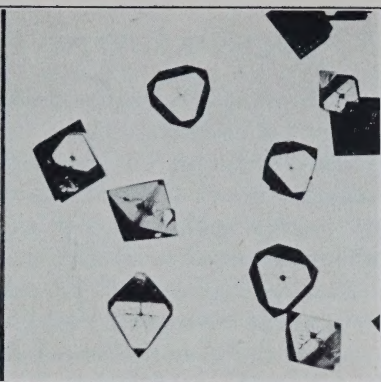


FIG. 41. Potassium with Chloroplatinic Acid. 100 $\times$.

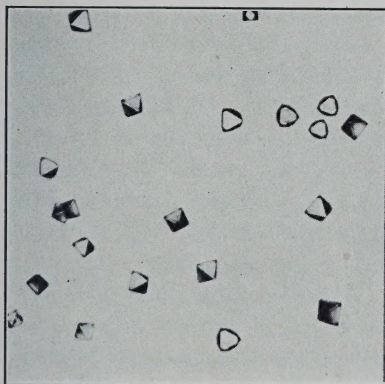


FIG. 42. Rubidium with Chloroplatinic Acid. 200 $\times$.

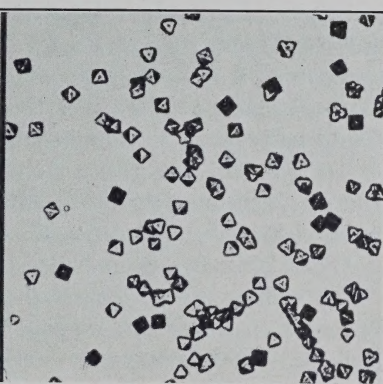


FIG. 43. Cesium with Chlorostannic Acid. 200 $\times$.

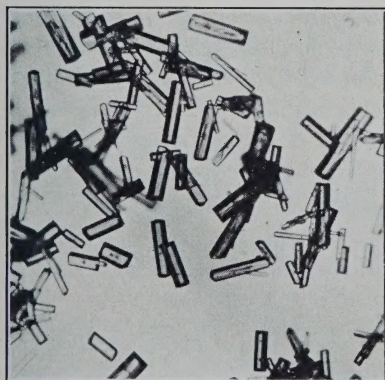


FIG. 44. Rubidium with Silver Chloride and Chlorauric Acid. 300 $\times$.

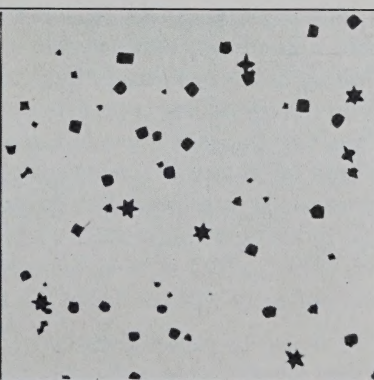


FIG. 45. Cesium with Silver Chloride and Chlorauric Acid. 300 $\times$.

crystallites and dendritic masses will be obtained instead of well-formed octahedra.

NH_4^+ , Rb^+ , Cs^+ , Tl^+ form with H_2PtCl_6 , salts having the same composition and habit as the potassium salt and isomorphous with it. The solubilities of these salts decrease in the order named, and under normal conditions the size of the crystals separating in a test drop decreases with the rise in the atomic weight of the element. (Fig. 42, page 67.) Cs_2PtCl_6 and Tl_2PtCl_6 are so insoluble that it is almost impossible to obtain a dilution which will allow the formation of octahedra that can be resolved without a magnification of about 200. Usually skeleton crystals only are obtained in the form of six-pointed stars.

Because of the relatively great difference between the solubility of K_2PtCl_6 and that of Rb_2PtCl_6 and Cs_2PtCl_6 it has been suggested that it is possible to differentiate between K^+ , Rb^+ , and Cs^+ by using a solution of K_2PtCl_6 as reagent. Theoretically it should be possible so to adjust the concentrations that a solution of K_2PtCl_6 will not give a precipitate with potassium salts but will at once precipitate rubidium, cesium, and thallium. In practice, however, this procedure is useless in dealing with material of wholly unknown composition.

The sodium salt $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ is so soluble that it rarely separates until the test drop has evaporated almost to complete dryness; it then appears as deliquescent yellow triclinic tabular prisms, or as thin plates exhibiting brilliant polarization colors. These prisms are so orientated upon the object slide that the observed extinction angle is about 22° .

The crystals of $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ are seldom well-formed, separate individuals, but occur in groups and aggregates at the periphery of the test drop; only the ends of the crystals projecting from the crystalline crust into the drop of liquid are well developed. Crushing the first crystals formed and drawing across the metastable solution will sometimes yield well-formed, separate prisms. This salt is so soluble that the addition of even strong alcohol will not induce crystallization.

$\text{Li}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$ is even more soluble than the sodium salt, and consequently will not appear in routine analyses.¹⁴

¹⁴ During the winter months the air is so dry in most of our American steam-heated laboratories that the chloroplatinates of sodium and beryllium, and sometimes even lithium, will separate.

$\text{BePtCl}_6 \cdot 8 \text{H}_2\text{O}$, though very soluble, may usually be induced to crystallize as the test drop goes to dryness. The crystals are characteristic, thin, well-formed, square or rectangular plates, rectangular prisms, or "octahedra" belonging to the tetragonal system (Fig. 51, page 81); although faintly yellow in color they appear to be colorless by transmitted light under the microscope.

K_2PtCl_6 and $(\text{NH}_4)_2\text{PtCl}_6$ differ so little in their solubilities that these two salts separate in crystals of the same size, appearance and color. Under the conditions which obtain in the tests, it is not possible to differentiate between them. Hence before deciding that potassium is present, ammonium must be proved to be absent. (See pages 74, 75.)

If NH_4^+ (NH_3) has been found, a little of the substance being analyzed is placed on platinum foil or in a tiny platinum cup and heated very carefully to dull red, no more, until all NH_3 has been expelled. Test for potassium in the residue. Or add NaOH and boil to expel the NH_3 . If NaOH is used make a "blank" to assure the absence of potassium.

When much sodium, lithium, beryllium, or magnesium is present, it is important that the reagent drop be large and concentrated and that the analyst assure himself that sufficient H_2PtCl_6 has been caused to flow into the test drop to provide sufficient $(\text{PtCl}_6)^{--}$ ions to satisfy all the cations present which can unite with $(\text{PtCl}_6)^{--}$ to form crystallizable salts under the conditions of the test.

Many organic compounds, such as amino compounds, substituted ammonias, alkaloids, etc., unite with H_2PtCl_6 to form crystalline compounds of relatively low solubility. Some of these give octahedral crystals of ammonium chloroplatinate or, as in the case of many alkaloids, crystals characteristic of the alkaloid will be obtained.

Experiments.

- (a) — Test KCl , NaCl , NH_4Cl with H_2PtCl_6 .
- (b) — Test a phosphate, a sulphate, and a tartrate of potassium.
- (c) — Test K_2SO_4 in the presence of much H_2SO_4 .
- (d) — Test RbCl , CsCl , TlNO_3 .

B-By Means of Perchloric Acid — HClO_4 .

Compound Formed — KClO_4 .

Apply the reagent by Method I, page 30.

When a drop of moderately concentrated HClO_4 flows into a drop of a cold dilute aqueous solution of a potassium salt there separate in a few seconds colorless orthorhombic prisms terminating in pyramids. The crystals separating from cold (*i.e.*, room temperature) solutions are better for identification purposes than those obtained in warm solutions.

In solutions concentrated with respect to K^+ ions dendritic masses and skeletal crystals are formed which bear no resemblance to the prismatic crystals of KClO_4 . Because of the low solubility of this salt these dendritic and skeletal forms almost invariably appear at first, and it is only after standing a minute or so that the well-formed crystals of characteristic habit are obtained.

The crystal forms which serve best to identify potassium are short stout prisms, resting on a prism face or rarely on a pyramid face, and thin plate-like rhombs which later develop into prisms. (Fig. 40, page 67.) There are also always formed rectangular plates and prisms, but since many other salts yield rectangular prisms, it is best to ignore them and depend upon the other types for the identification of potassium.

The crystals of KClO_4 are weakly birefringent, with negative double refraction and are only moderately refractive ($\beta = 1.47+$).

Rubidium, cesium, thallium (Tl^+), and ammonium form crystals having the same habit as the potassium salt and isomorphous with it.

Unlike the chloroplatinates and the chlorostannates the solubilities of these salts do not decrease with the rise in atomic weight.

If the solubility of KClO_4 is taken as 1, the relative solubilities of the perchlorates of the alkalis can be expressed thus; $\text{K}^+ : \text{Rb}^+ : \text{Cs}^+ : \text{Tl}^+ : \text{NH}_4^+ : \text{Na}^+ = 1 : 0.72 : 0.96 : 9.6 : 13.4 : 57.7$. These figures are only approximate. At room temperature, the solubility curves of the perchlorates of K^+ , Rb^+ , Cs^+ are substantially parallel, but rapidly diverge at higher temperatures.

The sodium salt $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ is probably more soluble than the above ratio shows, and its solubility varies greatly with the concentrations of other salts which may be present.¹⁵

The salt $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ separates below 52°C ., but at temperatures above 52°C ., the anhydrous salt NaClO_4 is obtained. Here again we find sodium at variance with the member of the potassium group.

¹⁵ Cornec and Dickety: *Bul. Soc. Chim.* **1927**, 1017.

LiClO_4 is hexagonal and very deliquescent.

KMnO_4 is isomorphous with KClO_4 . This is of considerable theoretical interest since manganese and chlorine are both members of Group VII, and should show a somewhat close relationship. Practical advantage is taken of this isomorphism to increase the delicacy of the reaction for K^+ ions and also the reaction for ClO_4^- . In the case of K^+ ions, sufficient NaMnO_4 is added to give the drop a deep pink color. Or in the absence of NaMnO_4 , "sodium manganate," a salt of very uncertain composition, can be employed, since in acid solution it changes over into permanganate with the precipitation of MnO_2 . Under these conditions, any crystals of KClO_4 which are formed take up KMnO_4 and become colored pink or dark rose. Since colored crystals are more easily detected in white light than colorless crystals the sensitivity of the reaction is apparently increased. In this case, however, the sensitivity of the reaction is actually increased, for it has been shown that the solubility of KClO_4 is lowered in the presence of KMnO_4 .

Permanganate ions, likewise, are taken up by crystals of Rb^+ , Cs^+ , NH_4^+ and Tl^+ perchlorates.

If a precipitate is obtained with HClO_4 , NH_4^+ , Rb^+ , Cs^+ , Tl^+ must be proved to be absent before the conclusion may be reached that K^+ is present. Recourse can be had to chemical tests or to optical constants to differentiate between this group. Since the test drop is usually acidified with HCl , Tl^+ ions need not concern us because of the low solubility of TlCl and its detection before HClO_4 is added.

When care is taken to test only dilute solutions the potassium group alone will be precipitated; all other perchlorates are too soluble to appear under the conditions which obtain in a properly performed test.

Although KClO_4 is insoluble in alcohol, the sensitivity of the test does not appear to be increased by exposing the test to alcohol vapors, nor is the separation of the crystals materially hastened.

The most satisfactory reagent is 70 to 72 per cent vacuum-distilled pure HClO_4 . Blank tests should be made to ascertain whether the acid has become contaminated by potassium from the glass container. NH_4ClO_4 may be used as a substitute for HClO_4 .

Many organic compounds, as for example alkaloids, yield with HClO_4 compounds of low solubility which may separate in well-formed crystals in concentrated test drops.

Experiments.

- (a) — Try the HClO_4 reaction with different salts of K.
- (b) — Introduce NaMnO_4 into the test drop, and test as above.
- (c) — Make a mixture of K and Na salts. Treat a drop of a solution of this material with HClO_4 , evaporate, treat with the reagent again, and again evaporate, extract the dry residue with alcohol, and test the alcoholic extract for sodium with $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$.
- (d) — Try the action of HClO_4 on members of the magnesium group, and upon members of the calcium group.

C—By Means of Bismuth Sulphate — $\text{Bi}_2(\text{SO}_4)_3$.

Compound Formed — $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$.

See Sodium, Method B, page 58.

When rough disks appear the conclusion is not always justified that some member of the potassium group is present. A decision should not be reached until sufficient time has elapsed to permit the formation of well-defined hexagonal plates.

It will be noted that the reaction product is believed to have the composition $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$. It is important to bear in mind this ratio of *three* molecules of potassium sulphate to *one* of bismuth sulphate, because it is often necessary to make several trials with different proportions of substance and reagent before a truly satisfactory crystallization can be obtained.

Too high a concentration of reagent and test substance gives rise to too rapid crystal formation and the separation of disks only.

Disks and plates on edge (Fig. 33, page 53; Fig. 34, page 61; Fig. 118, page 209) appear to be rectangular prisms with more or less rounded or beveled ends. These must not be confused with the characteristic prisms of the sodium salt (Fig. 32, page 53).

Rubidium, cesium and ammonium form double bismuth sulphates having the same habit as the potassium salt. The cesium salt may often, however, be readily recognized, because the hexagons are thicker and have their edges beveled with pyramid faces; these faces are very rare when potassium only is present.

D—By Means of Sodium Tartrate and Tartaric Acid — $\text{HNaC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O} + \text{H}_2(\text{C}_4\text{H}_4\text{O}_6)$.

Compound Formed — $\text{HKC}_4\text{H}_4\text{O}_6$.

Perform the test by Method III, page 34.

It is essential that the material to be tested be neutral, or at the most, only very slightly acid.

The dry film across which the reagent is to be drawn should be thicker than is usual in making tests by this method. This is done by evaporating to dryness one drop after another on the same spot.

The reagent consists of a rather concentrated solution of tartaric acid to which a small amount of sodium tartrate has been added. An excess of tartaric acid is used in order to assure the formation of the acid salt $\text{HKC}_4\text{H}_4\text{O}_6$, instead of the normal salt $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$, since the former is less soluble and its crystal form is more characteristic of potassium.

$\text{HKC}_4\text{H}_4\text{O}_6$ separates in short stout irregular orthorhombic prisms which are strongly birefringent but only moderately refractive. Hemihedral and skeletal forms predominate. Thin almost rectangular plates and tablets are also formed, which when viewed edge-wise appear to be slender prisms (Fig. 39, page 61).

Better and more reliable results are obtained when sodium tartrate is used in the reagent than when the test is made with tartaric acid alone. But if too much sodium salt is added there is danger of the formation of the double salt $\text{NaK}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$; this salt is not only less characteristic, but is more soluble than $\text{K}_2(\text{C}_4\text{H}_4\text{O}_6)$ and is over 200 times as soluble as $\text{HK}(\text{C}_4\text{H}_4\text{O}_6)$.

The Rb^+ , Cs^+ , NH_4^+ , and Tl^+ acid tartrates of the formula $\text{HM}(\text{C}_4\text{H}_4\text{O}_6)$ are isomorphous with the salt $\text{HK}(\text{C}_4\text{H}_4\text{O}_6)$. The rubidium and cesium acid salts are even less soluble than the potassium salt.

$\text{Rb}_2\text{C}_4\text{H}_4\text{O}_6$ and $\text{Cs}_2\text{C}_4\text{H}_4\text{O}_6$ are hexagonal (trigonal). $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ is monoclinic. These salts can be differentiated by their optical properties.

Although $\text{H}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6$ is isomorphous with $\text{HKC}_4\text{H}_4\text{O}_6$, the former salt usually separates, under the conditions of the test, in forms such that a close observer can distinguish between the two salts providing NH_4^+ and K^+ are not both present in the test drop under examination. These two acid tartrates can be differentiated by an observation of their optic axial angles, that of the ammonium salt being approximately half that of the potassium salt.

Many other elements form tartrates of low solubility, yielding crystals which may separate under the conditions that obtain in the test. These crystals, although of not the same habit as the

potassium salt, may bear a sufficiently close resemblance to it to lead to error unless checked on known material or by other methods. (See Fig. 70, page 113.)

Always study the preparations before they go to dryness, since double tartrates are almost invariably formed. There are so many possible combinations that it is almost impossible to become familiar with the crystal habits of all these salts, and as a result, their formation as the drop just goes to dryness is always puzzling to the analyst.

Sodium tartrate may be employed for the identification of calcium and to differentiate between strontium, barium, and lead. (See page 111.)

In some cases it is advantageous to mix in a centrifuge tube, the reagent, the solution to be tested, and an equal volume of 95 per cent alcohol. The mixture is allowed to stand for a short time and centrifuged. The crystalline precipitate collecting at the bottom of the tube is transferred to an object slide and examined under the microscope.

DETECTION OF AMMONIUM

Treatment of the Substance Prior to Making the Identification Test. — The radical ammonium functioning as the cation NH_4^+ so closely resembles the cations K^+ , Rb^+ , and Cs^+ in its behavior toward the reagents employed for the microscopic detection of the elements of Group I that no test can be regarded as truly specific unless applied to the NH_4^+ (*i.e.*, NH_3) set free from its salts and absorbed in a suitable manner.

The expulsion of NH_3 and subsequent fixation may be accomplished in a satisfactory manner by Method IX, page 40, employing the apparatus shown in Fig. 6, page 15.

The material to be tested is placed in the crucible, a drop of distilled water added and sufficient freshly ignited asbestos dropped in just to cover the solution. A drop of NaOH solution is added and the crucible immediately covered with an object slide carrying a hanging drop of dilute HCl . Gentle warming will expel the NH_3 , which will be "fixed" by the HCl .

NaOH , HNaCO_3 , CaO , or MgO may be used to set free the NH_3 , but KOH should not be employed on account of the risk of an apparently positive test due to spattering or creeping.

In the routine analysis of material of wholly unknown composition NaOH should be used, the use of the other reagents being restricted to examinations of special compounds where it may be desirable to employ a decomposing agent less energetic than NaOH. When only a very small amount of NH_3 is found in the condensate by the procedures described below, it is always essential that a "blank" test be made to assure reagent purity.

Finding NH_3 in the condensate is not necessarily proof of the presence of the ion NH_4^+ , since a number of nitrogen-containing organic compounds yield NH_3 when heated with NaOH, especially if an oxidizing substance is also present. In complex mixtures of this sort the identification of ammonium salts is by no means simple and often taxes the ingenuity of the analyst. Usually extraction with warm water and evaporation to crystallization will afford a fairly satisfactory separation of the water-soluble ammonium salts from the generally water-insoluble organic compounds. The identification of the crystalline residue obtained by evaporation may then be undertaken by chemical and optical methods.

Most ammonium salts sublime at moderately low temperatures, and with care satisfactory separations may be thus effected and crystalline sublimates obtained.

In the absence of the reagent H_2PtCl_6 it is better to have recourse to HIO_3 rather than testing with Mg^{++} and $(\text{PO}_4)^{---}$.

Experiments.

- (a) — Expel NH_3 from a mixture of NH_4Cl and KCl , and test the evolved gas with H_2PtCl_6 .
- (b) — Run a "blank" distillation with KCl alone.
- (c) — Test with HIO_3 (see Method B).
- (d) — Repeat the distillation, using urea and NaOH, and test for evolved NH_3 .

A—By Means of Chloroplatinic Acid — H_2PtCl_6 .

Compound Formed — $(\text{NH}_4)_2\text{PtCl}_6$.

The reagent is applied by Method I, page 30, to the solution of NH_4Cl , obtained by the expulsion of NH_3 by NaOH and fixation in HCl in the manner described above.

The H_2PtCl_6 test for ammonium is the quickest and most satisfactory at our command. When performed as directed upon expelled NH_3 it is subject to no errors and few interferences.

The highly refractive brilliant clean-cut octahedra grow to a

size easily recognized by low powers, and even if the concentration of NH_4Cl in the test drop is so high as to yield skeleton crystals of $(\text{NH}_4)_2\text{PtCl}_6$, these skeletons are sufficiently characteristic so that identification is certain. Moreover, recrystallization from hot water is always practicable. On the other hand, if a precipitate is not obtained, recourse to evaporation can always be had.

Although, as pointed out under potassium, the salt $(\text{NH}_4)_2\text{PtCl}_6$ is less soluble than K_2PtCl_6 , the two salts separate from solution on the object slide with exactly the same habit and of substantially the same size. (See Fig. 41, page 67.) The sensitivity of the reaction appears to be substantially the same for both NH_4^+ and K^+ ($0.4 \pm \mu$ gm.).

For a discussion of the characteristics and relationships of the chloroplatinates, see page 68.

Certain organic compounds that are volatile and water-soluble may appear in the hanging drop and yield a crystalline compound with H_2PtCl_6 , but the crystal habit of these compounds is not such as to be confused with $(\text{NH}_4)_2\text{PtCl}_6$.

B—By Means of Iodic Acid — HIO_3 .

Compound Formed — NH_4IO_3 .

When ammonium is to be tested for by this method, the NH_3 is expelled as usual with NaOH , but the crucible cover, instead of carrying a drop of HCl , is provided with a hanging drop of an approximately 10 per cent solution of HIO_3 .

The crucible is warmed very gently at intervals, so as to insure a slow expulsion and gradual absorption of NH_3 , and as a consequence, the slow growth of the crystals of NH_4IO_3 leads to the development of a characteristic habit and dimensions permitting easy recognition.¹⁶

Although this test is moderately sensitive (2μ gm.) the formation of characteristic crystals is slow and cannot be hurried.

The crystals of NH_4IO_3 (Fig. 50, page 81) usually appear first at the circumference of the hanging drop in the form of more or less dendritic masses made up of colorless, transparent, square, rectangular, or six-sided plates and prisms. The square and rectangular plates have the appearance of belonging to the cubic

¹⁶ Denigès: *Comptes rend.* **171**, 177 (1920).

Denigès and Barlot: *Bul. Soc. Chim.*, (4) **27**, 824 (1920).

system but are strongly birefringent, and according to Denigès are really monoclinic.

If instead of a 10 per cent solution of HIO_3 a very concentrated warm solution is employed, a series of acid iodates may be obtained whose composition depends upon conditions; some of these acid salts are metastable. Scratching the slide and breaking up the metastable salts leads to their transformation into stable forms.

Acid iodates of Na^+ have not been described, but NaIO_3 and several hydrated salts are known to be orthorhombic. The optical constants of the alkali iodates have not yet been determined.

Unless a definite concentration of the HIO_3 reagent is adhered to in the study of known and unknown material confusion may ensue, because of the formation and the separation of a series of compounds having different crystal habits and different optical constants.

Since the ion IO_3^- yields difficultly soluble crystalline salts with a number of cations, the test for ammonium should never be applied to a solution of the substance but must be made only by exposing a solution of HIO_3 to the gases expelled by gentle warming with NaOH .¹⁷

C-By Means of Magnesium Acetate — $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ and Sodium Phosphate — HN_3PO_4 .

Compound Formed — $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.

To the hanging drop upon the cover-slide obtained as suggested on page 41 (and which presumably contains NH_4Cl in acid solution) add a fragment of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{H}_2\text{O}$. Stir until all has dissolved. Add a fragment of $\text{HN}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$; stir thoroughly. If a precipitate appears, dissolve in the least possible amount of dilute HCl .

Into the test drop thus prepared, cause to flow a drop of NaOH of moderate concentration. In the presence of NH_4^+ , orthorhombic crystals of the salt $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ soon make their appearance.

Usually there is first formed a very fine granular or flocculent precipitate. This soon changes into large star-like and X-shaped skeletons that are very characteristic (Fig. 74, page 113). These

¹⁷ See Detection of the Alkaline Earths, page 119.

skeleton crystals in turn disappear by filling out into prismatic types.

In the change from skeleton to prismatic crystals there are formed thin plates with a rhombic or rectangular outline which, as they thicken, assume the appearance of a rectangular or a somewhat distorted envelop; these latter in turn thicken and become prismatic with faces recalling the roofs of houses (Fig. 75, page 113).

If the concentration of the test drop is very low with respect to NH_4^+ only the crystals of prismatic habit are seen. In such an event it is best to decant the mother liquor, dissolve the crystalline precipitate in the least possible volume of dilute HCl , and into this more concentrated test drop flow the NaOH . This procedure is suggested because the skeletons and dendrites passing into the prismatic crystals are the most characteristic phenomena exhibited by $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.

A triclinic salt $\text{H}_4(\text{NH}_4)_2\text{Mg}_3(\text{PO}_4)_4 \cdot 8 \text{H}_2\text{O}$ has also been described, but it is doubtful whether this salt can appear in the test drop under the conditions which have been outlined above.

In testing for ammonium, there may not be a sufficiently large amount of NH_4Cl present to prevent a separation of $\text{Mg}(\text{OH})_2$ or of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$, as heavy flocculent precipitates which fail to crystallize on standing, though in the case of the normal magnesium phosphate the formation of minute monoclinic needles is possible.

Although the salt $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ is of little value for the detection of NH_3 obtained by expulsion with NaOH , it is frequently met with by the analyst in plant and animal products, in culture media, etc. It is readily identified by its insolubility in cold water, moderate solubility in boiling water, and its immediate and complete solubility in HCl , from which it is reprecipitated by NaOH in the crystalline forms described above.

Moreover, this salt is of considerable theoretical as well as practical interest, for it is one of a group of isomorphous salts having the general formula, $N. M. \text{PO}_4 \cdot 6 \text{H}_2\text{O}$, in which N may be NH_4^+ , K^+ , Rb^+ , Cs^+ , but not Na^+ ; and M may be Mg^{++} , Fe^{++} , Mn^{++} , Co^{++} , Ni^{++} , and in which P can be replaced by As or V .

DETECTION OF RUBIDIUM AND CESIUM

These two elements differ so little from one another in their chemical behavior and are so closely related to potassium that their microscopic identification in complex mixtures is always exceptionally difficult.

Even when dealing with a relatively pure simple salt of rubidium or cesium, the differentiation is not easy, since in most tests dependence must be placed upon differences in solubility alone. Attention has already been called to the fact that identity tests based wholly upon differences in solubility require exceptional skill, experience and judgment on the part of the analyst, and he must form an opinion largely through inference. The microscopical identification of rubidium and cesium in mixtures is therefore always open to more or less uncertainty.

In all problems involving the recognition of rubidium and cesium recourse should be had to the spectroscope or spectrograph.

The following reactions may be employed in distinguishing between Rb^+ and Cs^+ .

A—By Observation of the Differences in the Solubilities of Rb_2PtCl_6 and Cs_2PtCl_6 .

The solubility of the different alkali chloroplatinates rapidly decreases with the rise in the atomic weight of the cation.

If a drop of a concentrated solution of H_2PtCl_6 is caused to flow into an exceedingly dilute solution of salts (chlorides) of the alkali metals, Rb_2PtCl_6 and Cs_2PtCl_6 will be almost instantly precipitated as skeletal crystals or as minute octahedra, but crystals of corresponding salts of potassium or ammonium will not appear until the concentration is very much higher and the sodium salt will not separate until the preparation passes substantially to dryness.

The size of the crystals formed and the limiting values for their almost instantaneous precipitation offer a method for differentiating between potassium, rubidium, and cesium. The elimination of potassium from the problem is fairly simple by comparing the behavior of the unknown material with "blank" tests containing KCl. If to a series of test drops of varying concentrations of the unknown and drops of KCl of as nearly as possible the same concentration and degree of acidity (with HCl), in each

different set of drops, H_2PtCl_6 is added, and a precipitation of tiny yellow octahedral crystals is obtained in the drops of the unknown *after* the corresponding dilution drops of KCl have failed to yield a separation of chloroplatinate crystals, and the crystals obtained with the unknown are *smaller* than experience has shown are to be expected with potassium, the assumption is justified that rubidium or cesium (or a mixture) is present and not potassium.

The same method of procedure may then be adopted to differentiate between rubidium and cesium.

This method of attack (which is Method IV, page 35) may often be applied to mixtures with good results; but it must be borne in mind that if, in the drops of the solution of the unknown, there are materials which will affect the solubility or alter the characteristic habit of the alkali chloroplatinates, the results of the test are valueless so far as identification of the cation is concerned.

The differentiation between Cs^+ and Tl^+ is not possible by this method.

A variant of the above "dilution" method consists in adding to the test drop a drop of a saturated solution of K_2PtCl_6 , on the principle that this reagent will not cause a precipitate in a *dilute* solution containing K^+ , but an immediate precipitate will result if Rb^+ or Cs^+ (or Tl^+) are present.¹⁸

B—Observation of the Difference in the Solubilities of the Silicomolybdates of Rubidium and Cesium.

The difference in the solubilities of the silicomolybdates of rubidium and cesium is sufficiently great to permit differentiation by having recourse to the dilution method discussed under A (page 79).

The most satisfactory results appear to be obtained when the reagent is applied by Method III, page 34. The dry film should be *exceedingly thin* and prepared from an *excessively* dilute solution. The reagent consists of a dilute solution of ammonium silicomolybdate acidified with a trace of HNO_3 . This very dilute solution is drawn across the dry film and then *at once* a drop of a concentrated solution of the reagent is added in the same place and the object slide slightly tilted so as to cause the concentrated reagent to flow into the channel and across the test drop.

If rubidium is present, there will appear, along the edges of the

¹⁸ See Gravestine: *Emich Festschrift*, p. 135 (*Mikrochemie*, 1930).

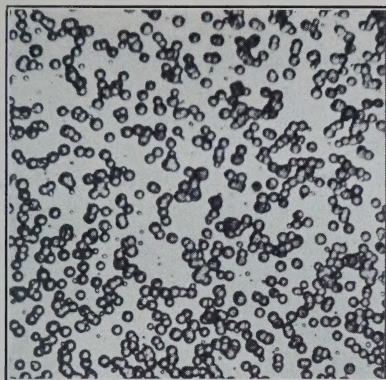


FIG. 46. Rubidium with Sodium Silicomolybdate. 300 $\times$.

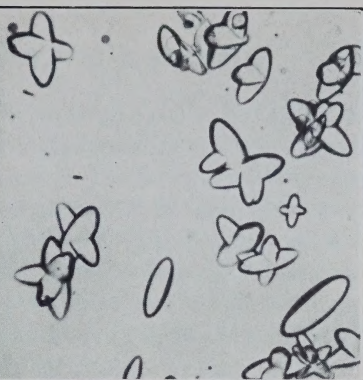


FIG. 47. Lithium with Disodium Phosphate. 200 $\times$.



FIG. 48. Lithium with Ammonium Carbonate. 100 $\times$.

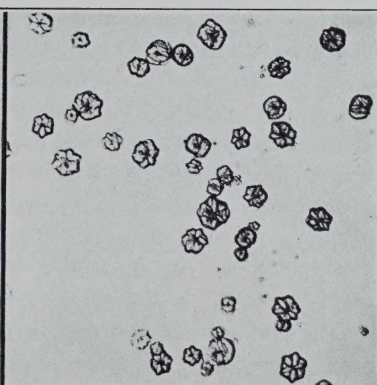


FIG. 49. Lithium with Ammonium Carbonate. 200 $\times$.

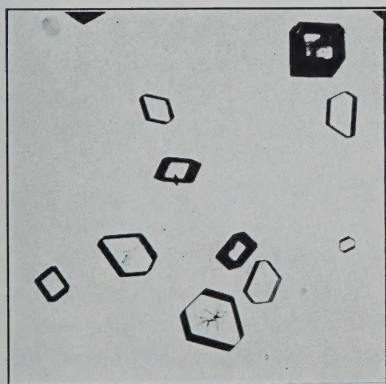


FIG. 50. Ammonium with Iodic Acid. 100 $\times$.

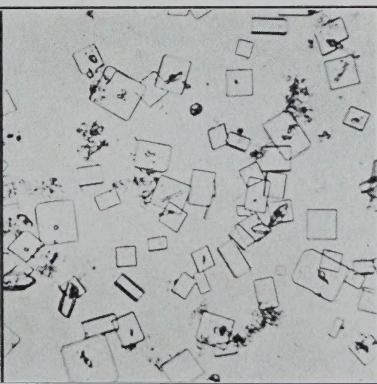


FIG. 51. Beryllium with Chloroplatinic Acid. 200 $\times$

channel, tiny, lemon-yellow, darkly contoured, spherical crystals sometimes resembling octahedra and cubes with more or less rounded angles. Most of these crystals appear to be spheroidal and their crystal faces can be discerned only by careful illumination and focusing (Fig. 46, page 81). Tiny, three-, four-, and six-armed skeletal crystals are also formed in abundance. The composition of this salt has not been established definitely, but the formula $\text{Rb}_4\text{Mo}_{12}\text{SiO}_{40} \cdot 14 \text{H}_2\text{O}$ has been proposed.

In the case of cesium salts tested in this manner only a very fine granular precipitate is obtained. Even high magnifications fail to reveal more than rounded grains and minute disks.

The potassium salt is quite soluble and may appear as well-formed prisms of considerable size. The salts of sodium and lithium are too soluble to separate under the conditions of the test.

Ag^+ , Tl^+ , and Hg^+ and also the ions of the magnesium and the calcium groups yield difficultly soluble silicomolybdates, but if the test has been performed as described, these ions will not interfere with the identification of rubidium and cesium.

Better formed crystals of rubidium silicomolybdate can be obtained by adding a dilute solution of the reagent to a dilute solution of the rubidium salt, but this method of testing does not yield as sharp a differentiation between rubidium and cesium.

The presence in the test drop of a moderate concentration of ammonium salts is objectionable, as there is then danger of the separation of crystals of the salt $(\text{NH}_4)_4 \cdot \text{Mo}_{12}\text{SiO}_{40} \cdot 8 \text{H}_2\text{O}$ (?).

C—By Means of Chlorostannic Acid — H_2SnCl_6 .

Compounds Formed — Rb_2SnCl_6 or Cs_2SnCl_6 .

When tin is dissolved in HCl and the solution boiled in the presence of oxygen (air) SnCl_4 is formed, and if an excess of strong HCl is present, we may regard the compound present in solution as H_2SnCl_6 . This constitutes the reagent for members of the potassium group.

The reagent should be added to very dilute test drops only. Acidification with HCl is desirable and the best results are obtainable when the reagent is added by Method I, page 30.

Freshly prepared solutions of H_2SnCl_6 are preferable to solutions obtained by dissolving crystalline SnCl_4 in water.¹⁹

¹⁹ Stannic chlorides of commerce are usually mixtures. They correspond to the formula $\text{SnCl}_4 \cdot x\text{H}_2\text{O}$, where x may be 3, 5, or 8. All three salts are

Cesium is instantly precipitated as Cs_2SnCl_6 in the form of very tiny colorless highly refractive regular octahedra and cubes (Fig. 43, page 67; Fig. 102, page 169). The salt is so difficultly soluble that even in very dilute solutions the crystals formed usually require a magnification of at least $200\times$ for their resolution. Not infrequently Cs_2SnCl_6 is precipitated as masses of skeletal crystals. Under these conditions the crystals are very much larger and cannot be distinguished from skeletal crystals of Rb_2SnCl_6 . Skeleton crystals are not formed if the dilution of the test drop has been sufficiently great.

Tl_2SnCl_6 is even less soluble than Cs_2SnCl_6 and is therefore always precipitated in exceedingly minute cubes, octahedra, or in skeletal forms. The crystals are colorless and highly refractive.

Rb_2SnCl_6 also forms colorless octahedra, but because of the higher solubility of the salt the crystals are much larger than those of cesium.

K_2SnCl_6 forms relatively large colorless octahedra whose solubility is so much greater than that of either Cs_2SnCl_6 or Rb_2SnCl_6 that there is little danger of confusing potassium with rubidium or with cesium; but if much strong HCl is present differentiation becomes impossible. The ammonium salt differs but little from the potassium salt in solubility.

The chlorostannate of sodium and that of lithium are so soluble that they will not appear until the test drop passes to dryness. Both these salts are hydrated, and of uncertain composition. Neither one crystallizes in the cubic system.

Thus far anhydrous chlorostannates only have been prepared of ammonium, rubidium and cesium. But potassium forms $\text{K}_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$ (orthorhombic) below 25°C .; above 25°C . the anhydrous salt is formed, nevertheless at room temperature upon an object slide the anhydrous salt separates. The potassium salts readily hydrolyze if boiled in concentrated solutions containing little or no free HCl .

All attempts to prepare chlorostannates of Ag^+ , Cu^+ or Au^+ have thus far failed.

The difference in the solubilities of the cesium and rubidium monoclinic. Old samples of stannic chloride are usually basic and do not dissolve completely in dilute HCl . Such samples should be heated with aqua regia, the excess of acid driven off and the resulting clear solution employed as reagent.

chlorostannates is sufficiently great to enable an experienced analyst to distinguish between them, especially if the dilution method described on pages 79, 80 is followed.

Ammonium salts should be absent; they can be removed by ignition or treatment with NaOH.

The sensitivity of the reaction can be measurably increased by adding to the test drop a fragment of NaI, thus causing the formation of yellow iodostannates. The increase in sensitivity is due to two causes: lowering of solubility, and production of a colored compound. The yellow-colored salt is probably a solid solution of Cs_2SnI_6 in Cs_2SnCl_6 .

In the presence of much Fe^{+++} the chlorostannates are colored yellow.

For a further discussion of the chlorostannates and allied salts, see Tin, page 177.

Since the reagent contains Cl^- ions, any compounds present precipitable by Cl^- will separate in the test drop unless HCl has been added to the solution of the unknown before the application of the chlorostannic acid. Silver, unless removed, may under favorable conditions yield colorless highly refractive cubes and octahedra of AgCl. For other possible compounds appearing as precipitates when HCl is added, see page 364.

D—By Means of Silver Chloride, AgCl, and Chloroauric Acid, HAuCl_4 .²⁰

Compounds Formed — $6 \text{RbCl} \cdot 2 \text{AgCl} \cdot 3 \text{AuCl}_3$ or
 $2 \text{CsCl} \cdot \text{AgCl} \cdot \text{AuCl}_3$.

To a very dilute solution of auric chloride in strong HCl, add a small quantity of the material to be tested. Stir thoroughly. If crystals of difficultly soluble chloroaurates appear, dilute the drop and warm gently until the crystals disappear. Into the test drop thus prepared introduce a very little freshly precipitated AgCl (or a fragment of AgNO_3). Allow the preparation to stand at room temperature for several minutes, then transfer to the stage

²⁰ Emich: *Monats.* **39**, 775 (1918); **41**, 243 (1920); **46**, 261 (1925).

Bayer: *Monats.* **41**, 223 (1920).

Vogel: *Monats.* **46**, 265 (1925).

Martini: *Mikrochemie*: **8**, 231 (1929).

Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. III, pp. 594–595.

of the microscope. If no reaction is obtained, crush a fragment of the material being tested in the center of one of the masses of AgCl.

If rubidium is present, the AgCl becomes covered with tiny, wine-red, blood-red, or brownish-red crystals, but if cesium is present the white masses of AgCl become covered with a very fine jet-black granular film.

Crush the AgCl masses, together with the adhering crystals, thus "seeding" the preparation. In a few minutes the chloroaurates will have crystallized throughout the drop.

The cesium silver chloroaurate $2\text{CsCl}\cdot\text{AgCl}\cdot\text{AuCl}_3$ is quite insoluble and is therefore mostly precipitated in a very finely divided condition; but in preparations which have stood for some little time definite crystals can be found in the form of jet-black squares, hexagons, triangles, and four- and six-pointed stars (Fig. 45, page 67). A magnification of $150\times$ or over is required to disclose their shape.

The more soluble rubidium salt $6\text{RbCl}\cdot 2\text{AgCl}\cdot 3\text{AuCl}_3$ makes its appearance after most of the cesium salt has separated. Unlike the cesium salt it crystallizes in well-developed orthorhombic plates and prisms of sufficient size to be readily identified with a 16-mm. objective. The prisms usually have square ends, but sometimes terminate in angles of 60° to 65° . They show a marked tendency to twin and to form masses of radiating slender crystals (Fig. 44, page 67). In color they range from a yellowish-red in thin plates to a deep reddish-mahogany in thick prisms, and may even be so dark as to appear almost black. This compound has a high index of refraction, the crystal faces are brilliant reflecting surfaces and show a play of spectral colors.

This interesting reaction affords an easy method of differentiating between potassium, rubidium, and cesium, providing that comparatively pure salts are dealt with *and that ammonium salts are absent*.

With salts of ammonium there is often at first obtained a separation of tiny jet-black granules that cannot be distinguished from the cesium reaction. Later orthorhombic prisms appear which in habit and color correspond to the rubidium salt. Wells²¹ has shown that the ammonium salt has the formula $6\text{NH}_4\text{Cl}\cdot 2\text{AgCl}\cdot 3\text{AuCl}_3$. It is thus similar to the corresponding salt of rubidium.

No crystalline precipitate is obtained with sodium or potassium,

²¹ Wells: *Amer. J. Sci.* (5) **3**, 257, 315 (1922); (5) **4**, 476 (1922).

but in concentrated solutions the AgCl may become peptized and turn black in such a manner as to necessitate very careful observation to avoid falling into the error of concluding that cesium is present.

Even if the preparation is allowed to stand until the test drop has evaporated to dryness, the double chloroaurates are still easily differentiated. The cause of the color of these compounds has not yet been satisfactorily accounted for.

If the solution of AuCl_3 is not sufficiently dilute, simple chloroaurates are apt to separate in crystalline form. This is especially true of the alkali chloroaurates; the solubilities of these salts expressed in grams per 100 grams of water at 20° are as follows: Li^+ 57.7; Na^+ 60.2; K^+ 38.2; Rb^+ 9.0; Cs^+ 0.8. It is obvious that in testing by this method simple chloroaurates are almost sure to be precipitated as well as the double chloroaurates.

Calcium, strontium and barium form chloroaurates of the general formula $M(\text{AuCl}_4)_2 \cdot 6 \text{H}_2\text{O}$; the Mg group yields $M(\text{AuCl}_4)_2 \cdot 12 \text{H}_2\text{O}$ or $M(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$; Mn^{++} gives $\text{Mn}(\text{AuCl}_4)_2 \cdot 12 \text{H}_2\text{O}$ or $\text{Mn}(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$, Co^{++} and Ni^{++} $M(\text{AuCl}_4)_2 \cdot 8 \text{H}_2\text{O}$. The crystallography of none of these compounds has been definitely established.

By substituting I for Cl in the gold reagent there is obtained iodoauric acid, which has been recently shown to yield specific reactions for the potassium group of metals.²²

If a drop of a mixture of HAuI_4 and AgI in HI is caused to flow into a test drop containing members of the potassium group, there will be formed double iodoaurates of as yet unknown composition. The potassium salt separates as black slender acicular crystals, singly and in groups and bundles. Ammonium gives black curving brush-like aggregates that soon disintegrate. Rubidium forms black irregular four-sided plates, and cesium yields black vermiform aggregates, crosses, rods, and hexagons.

Unfortunately, the reagent necessary for these interesting reactions is not easily prepared and is very unstable, hence the test is impracticable in routine qualitative analysis.

If instead of HAuCl_4 , chlorostannic acid H_2SnCl_6 and AgCl are used, very insoluble chlorostannates of silver and rubidium and

²² Burkser and Rublof: *Mikrochemie* 5, 137 (1927).

Gravestein: *Emich-Festschrift*, p. 140, suggests using AgI in NaI as a specific test for Cs.

cesium are obtained, and in this case the difference in the solubilities of the rubidium and cesium salts appears to be even greater than in the case of the gold salts. Unfortunately, these reactions cannot be used to good advantage in microscopic qualitative analysis.

DETECTION OF LITHIUM

The microscopic identification of lithium is practicable only in materials in which lithium is present in relatively high concentrations. This restricts the application of the tests to comparatively pure salts, very simple mixtures, or to material in which lithium has been concentrated by extraction and separation methods, *e.g.*, conversion into chloride or bromide, and extraction of the dry residue with one of the higher alcohols in which LiCl is quite soluble, but in which most other chlorides and bromides are difficultly soluble or quite insoluble.

Lithium is best identified by the flame spectrum of its chloride $\text{Li}\alpha = \lambda 6708$.

Not only have we no good chemical tests for this element, but there are few salts of lithium that crystallize sufficiently well to permit a satisfactory determination of their optical constants when crystallized upon an object slide.

Lithium can be differentiated from the alkali metals in that it forms a difficultly soluble phosphate and carbonate. Its easily soluble sulphate readily distinguishes it from the sulphates of the alkaline earths.

The salts of lithium, as a general rule, resemble those of sodium more than those of the other alkali metals, in that the perchlorate, chloroplatinate, chlorostannate, tartrate, triple chloride (Li, Ag, Au), picrate, and silicomolybdate are all so soluble as not to separate under the conditions which obtain in the testing for members of the potassium group.

Unlike sodium, lithium yields no double acetate of low solubility with UO_2^{++} , nor does it form a triple acetate with UO_2^{++} and certain bivalent elements, nor a difficultly soluble double sulphate with bismuth. Its fluosilicate is more soluble than that of sodium, and it is almost impossible to induce lithium to form an "alum" upon an object slide.

With the possible exception of LiF there are therefore no "crys-

tal reactions" which link lithium with Group I. The relatively low solubility of lithium carbonate and of lithium phosphate throws lithium into Group II with the alkaline earths. But lithium differs from magnesium in that its double phosphate with ammonium $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ is soluble in ammoniacal solutions. Unlike calcium, strontium, and barium, the sulphates and oxalates of lithium are quite soluble.

All the above facts relative to the analytical behavior of lithium must be borne in mind whenever analyses are to be made of materials in which lithium may possibly be present.

A-Identification by Means of Disodium Phosphate — $\text{HN}_2\text{PO}_4 \cdot \text{H}_2\text{O}$.

Compound Formed — $\text{Li}_3\text{PO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$.

The solution to be tested should be concentrated with respect to lithium and must be neutral, or better, very slightly alkaline. The reagent is added by Method I, page 30, and the preparation heated almost to boiling. A granular precipitate of $\text{Li}_3\text{PO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ appears at once. This precipitate when examined at $200\times$ is seen to consist of highly refractive lenticular and fusiform crystals, singly or in crosses or in star-like groups or irregular radiating clumps (Fig. 47, page 81). Sheaves, bundles, and more or less spherical masses of exceedingly fine crystals are sometimes formed. The fusiform and acicular crystals extinguish in the direction of their elongation. The spherulites show the usual black cross between crossed nicols. This salt is dimorphic, forming crystals belonging either to the orthorhombic system or to the hexagonal system.

Only the fusiform crystals are to be regarded as characteristic of lithium.

If the solution to be tested is acid, evaporate to dryness to drive off the excess of acid, then neutralize with *very dilute* NaOH , using great care *not to exceed* a mere trace of alkalinity. Neutralization by means of NH_4OH is to be avoided since the salt $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ is apt to be formed, thus preventing the precipitation of tri-lithium phosphate; for the same reason ammonium salts should be absent.

It is therefore important that a test for the presence of ammonium (NH_3) shall be made before testing for lithium. If NH_3 is found, drive it off by ignition or by expulsion with NaOH .

The ready solubility of $\text{NH}_4\text{Li}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$ may be turned to good account when doubtful tests are obtained. The supernatant liquid is decanted from the precipitated phosphate (or filtered), the residue is washed and then dissolved in the least possible amount of very dilute HCl . To this clear solution NH_4OH is added. If no precipitate appears, the precipitate may have been lithium phosphate, but if a precipitate appears, members of Group II or other groups higher in the periodic series are present.

B-Identification by Means of Ammonium Carbonate — $(\text{NH}_4)_2\text{CO}_3$.

Compound Formed — Li_2CO_3 .

Add the reagent by Method II, page 32, to a neutral solution of the material to be tested. As in all tests for lithium the drop must be concentrated with respect to this element.

Li_2CO_3 is not precipitated at once, but after a few minutes separates in the form of globulites, bristly masses, and sheaf-like bundles of acicular monoclinic crystals. More or less irregular thin plates are also formed. All these crystals, especially the aggregates, vary with the concentration of the test drop (Figs. 48, 49, page 81). Hence care and experience are required both in judging the proper concentration and in the interpretation of the results obtained. When in doubt perform a test upon a known lithium salt, duplicating the conditions, as far as possible, in the "blank" and the test drop.

This reaction is characteristic only when applied to comparatively pure salts of lithium. It is generally unsatisfactory and unreliable when applied to complex mixtures.

Calcium is precipitated in tiny, sparkling, strongly birefringent disks and rhombs, which cling tightly to the glass of the object slide and permit easy decantation of the mother liquor and subsequent identification of the crystals by other reagents. The crystals of CaCO_3 are usually hexagonal rhombohedral, but are sometimes orthorhombic.

Strontium yields spherulites of SrCO_3 , often of considerable size; these spherulites are usually incompletely filled out, producing sheaf-like or dumb-bell aggregates.

Barium forms tiny spherulites, fusiform bundles and sheaf-like aggregates not readily distinguished from the similar aggregates of strontium.

In the high concentrations required for the separation of Li_2CO_3 , the alkaline earths give only fine granular precipitates, the forms just described being absent.

$(\text{NH}_4)_2\text{CO}_3$ is used as reagent rather than HNaCO_3 so as to avoid the separation of the zinc double salt (see Zinc, page 132) or the formation of a double sodium calcium carbonate.

One of the most serious drawbacks of the carbonate test for lithium is that the concentrations required are so high that many salts are apt to crystallize in the test drop, thus masking the lithium test. Moreover, it is very difficult so to control conditions that only Li_2CO_3 is formed. No less than eleven hydrated carbonates of Li_2CO_3 have been described, but it is probable that many of these are mixtures. The salt HLiCO_3 exists in solution only.

Magnesium interferes seriously with the carbonate test for lithium or the alkaline earths, and it is to be expected that the test may fail in the presence of any element yielding an insoluble or difficultly soluble carbonate or forming an insoluble hydroxide.

Under certain conditions the crystals of Li_2CO_3 bear a striking resemblance to sheaves of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Both are monoclinic. Since $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is much more soluble in acid than in neutral or alkaline solution it may happen that the addition of $(\text{NH}_4)_2\text{CO}_3$ may cause a precipitation of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ in bundles of fine acicular crystals.

OTHER TESTS FOR MEMBERS OF GROUP I

The following tests, although of very little value in the analysis of complex materials of the sort which commonly come to chemists for examination, may nevertheless be of considerable value in special cases.

Since these tests are limited in their application only a brief description is given of each.

Sodium, by Means of Potassium Pyroantimonate — $\text{H}_2\text{K}_2\text{Sb}_2\text{O}_7 \cdot 6 \text{H}_2\text{O}$ (?)

Compound Formed — $\text{H}_2\text{Na}_2\text{Sb}_2\text{O}_7 \cdot 6 \text{H}_2\text{O}$ (?)

Apply a saturated solution of the reagent by Method I, page 30, to a neutral, moderately concentrated, test drop.²³

Tiny elliptical plates and fusiform crystals are formed, uniting

²³ See also Böttger: *Pregl Festschrift*, p. 16 (*Mikrochemie*, 1929).

in crosses, stars, or globular masses (Fig. 37, page 61). From dilute solutions non-characteristic tetragonal tetrahedra, cubes, and octahedra separate. No precipitate is obtained with Rb^+ , Cs^+ , or NH_4^+ but much NH_4^+ interferes. Li^+ and Mg^{++} give hexagons (Fig. 38, page 61). Alkaline earths and many heavy metals give rise to "amorphous" precipitates.

Experiments.

(a) — Try the reaction with potassium antimonate on salts of Na in both dilute and concentrated solutions.

(b) — Try the reagent on NH_4 salts alone and then in a mixture of Na and NH_4 salts.

(c) — Try the reagent on a salt of Mg; a salt of Ba.

Sodium, by Means of Cerous Sulphate — $\text{Ce}_2(\text{SO}_4)_3$.

Compound Formed — $\text{Na}_2\text{SO}_4 \cdot \text{Ce}_2(\text{SO}_4)_3 \cdot 2 \text{H}_2\text{O}$.

Apply the reagent by Method I, page 30. Very tiny lenticular grains, fusiform bodies, and dumb-bell-shaped aggregates are obtained with sodium.

These crystals are characteristic but require a very high magnification for their resolution. Potassium gives hexagonal plates or spherical masses. To obtain good results the preparation should be gently warmed at the zone of union of reagent and test drop. It is important that the reagent be cerous and not ceric sulphate nor a mixture of the two.

Potassium, by Means of Picric Acid — $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$.

Compound Formed — $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$.

Apply an alcoholic solution of the reagent by Method V, page 36.

Long, yellow, characteristic, acicular crystals or long, tapering, prism-like forms are obtained. The reagent is dissolved in dilute alcohol and sufficient water added to prevent the drops, when placed on the object slide, from flowing over the glass.

Picric acid crystallizes in orthorhombic prisms very different from those of the potassium salt.

The sodium and lithium salts are too soluble to give a reaction.

Rubidium and cesium give crystals closely resembling those of potassium. Ammonium may yield long acicular crystals but more often long thin plates; these crystals may be either yellow or reddish; the latter are strongly pleochroic. Ti^+ behaves like

K^+ but the crystals are smaller; a yellow and a red form are known.

Picric acid forms crystallizable picrates with a large number of elements and organic compounds, hence the usefulness of this reaction for the potassium group is greatly restricted.

Potassium, by Means of Sodium Cobaltinitrite — $Na_3Co(NO_2)_6$.

Compound Formed — $K_3Co(NO_2)_6 \cdot 1\frac{1}{2} H_2O$.

Apply a solution of sodium cobalt nitrite by Method I, page 30. An exceedingly fine granular precipitate is formed, too finely crystalline to be of value in the analysis of complex mixtures. NH_4^+ , Rb^+ and Cs^+ give a like reaction.

By Means of the Triple Nitrite Reaction, see Lead, page 184.

By Means of Chlorostannic Acid — H_2SnCl_6 — see page 82.

Lithium, by Means of Ammonium Fluoride — NH_4F — see page 63.

Lithium fluoride crystallizes in cubes and other forms of the cubic system. This reaction is not characteristic, but because LiF is less soluble than NaF or KF the reaction is a useful one.

GROUP I. SEPARATION METHODS

It sometimes happens that the alkali metals are combined in compounds of such a nature that the direct application of the identity tests are unsatisfactory or misleading, especially when a quantitative "estimate" is important. Under such conditions a separation of the alkalis from the alkaline earths, heavy metals, or complex ions is imperative. The following procedures are suggested as means of avoiding possible errors.

I—The cations present are combined with volatile inorganic anions. — Several large drops of the aqueous solution are placed in a platinum cup. Solid oxalic acid²⁴ is added in the proportion of about ten times the weight of the material in solution. The preparation is heated gently until all water has been driven off, great care being exercised to avoid spurting and decrepitation. The temperature is now slowly raised until the oxalic acid sub-

²⁴ Maljaraff: *Mikrochemie* 6, 92 (1928).

limes and the heating is continued until sublimation ceases. Usually it is necessary to repeat this treatment at least twice. The temperature is finally raised to a red heat.

The alkalis and the alkaline earths are thus converted into carbonates; magnesium and the heavy metals into oxides.

The mass is extracted with hot water, using as small an amount as possible; the alkali carbonates pass into solution (with part of the lithium). The aqueous solution is evaporated to dryness and portions tested.

If lithium is to be searched for, the residue insoluble in water is dissolved (or extracted) with HCl, the solution evaporated to complete dryness, extracted with isoamyl alcohol and the alcoholic extract evaporated and tested for lithium.²⁵ If much material is extracted by the alcohol it may be necessary to precipitate an aqueous solution with Ba(OH)₂. Filter, treat the filtrate with HCl; evaporate to dryness; extract the dry residue with isoamyl alcohol; evaporate the alcoholic extract and test the residue for lithium.

II—Separation of the alkalis from materials containing non-volatile inorganic anions (Behrens-Schoorl).—To the aqueous solution add BaCl₂ or Ba(OH)₂ in slight excess; filter or centrifuge; to the clear filtrate add (NH₄)₂CO₃ to remove the barium; filter or centrifuge. Acidify the filtrate with HCl; evaporate to dryness and ignite to drive off all ammonium salts.

Extract the dry residue with isobutyl or isoamyl alcohol, warming gently to assist solution of the lithium (and thallium). Evaporate the alcoholic extract and test the residue for lithium with HF and with HNa₂PO₄. Test for thallium with KI or AuCl₃.

The material insoluble in alcohol is tested for:

Na⁺ with Zn(C₂H₃O₂)₂·UO₂(C₂H₃O₂)₂.

K⁺ with H₂PtCl₆ or HClO₄ (NH₄⁺ must be absent).

Rb⁺ with H₂PtCl₆ (or K₂PtCl₆) and also with AgCl + AuCl₃.

Cs⁺ with H₂PtCl₆ (or K₂PtCl₆) and also with AgCl + AuCl₃.

²⁵ Or the dry residue may be extracted with acetone, Caley: *Ind. Eng. Chem. (Anal. Ed.)* **2**, 304 (1930).

According to Sinka: *Zeit. anal. Chem.* **80**, 430 (1930), lithium salts are soluble in anhydrous diethylene dioxide but salts of sodium and potassium are insoluble.

III—Detection of the alkalis in silicates, glass, etc. — The material is crushed in a “diamond” mortar and rubbed into an impalpable powder in an agate mortar. Decomposition is effected by treatments with NH_4F and HCl (1 : 1) or with HF and HCl at room temperature. Examine the preparation for crystals of Na_2SiF_6 and NaCl (KCl , RbCl , CsCl).

Treat repeatedly with HF (or NH_4F) and concentrated HCl , heating to expel SiF_4 . (Treatment with HF and H_2SO_4 is better.) Fume off the excess of acid, and ignite to expel ammonium salts if NH_4F has been used.

Extract the residue with warm water. The solution may contain Na^+ , K^+ , Mg^{++} , Ca^{++} . Test separate portions for these cations.

If Rb^+ , Cs^+ , Tl^+ , Li^+ are to be searched for, heat the residue after the expulsion of fluorine and fluorides, as described in I and II, according to whether HCl or H_2SO_4 has been used.

CHAPTER IV

THE DETECTION OF THE ELEMENTS OF GROUP II

Be; Ca, Sr, Ba; Mg, Zn, Cd; Hg

The element beryllium, heading Group II, like all the other elements of lowest atomic weight in each of the first seven vertical groups of the Periodic System, is transitional in its chemical properties. In most of its compounds beryllium resembles magnesium and zinc, but in others the resemblance to aluminum is more marked than that to magnesium. Its sulphate is not isomorphous with magnesium sulphate.

Because of its marked transitional character beryllium can give rise to crystalline compounds which may make their appearance in testing for the presence of Group I, Group II, or Group III. Its salts are colorless and lack characteristic features; hence the microscopical detection of beryllium in mixtures is usually difficult, unsatisfactory, and often impossible.

Like the alkalis beryllium forms a crystalline chloroplatinate. (See Potassium, pages 68, 69.)

Unlike magnesium, zinc, and cadmium, beryllium does not readily form a triple acetate with sodium and uranyl; even if these cations and anions are present in the proper concentration to produce the triple salt it will not separate until the preparation has evaporated to dryness.

Salts of beryllium are precipitated by NaOH and KOH, $\text{Be}(\text{OH})_2$ being formed. This compound is soluble in an excess of alkali because of the formation of a berylate $\text{Be}(\text{ONa})_2$ or $\text{Be}(\text{OK})_2$. In this respect beryllium resembles zinc (cadmium), and the aluminum group; but unlike aluminum, beryllium hydroxide is soluble in NH_4OH . Beryllium does not form "alums." Most salts of beryllium are hydrolyzed if their aqueous solutions are boiled.

In dilute solutions of beryllium salts, oxalic acid produces no precipitate (distinction from the scandium group of Group III), but in concentrated solutions beryllium forms a readily crystallizable oxalate of sufficiently low solubility to separate in a test

drop; in this it resembles calcium, strontium, and barium. Its relation to the primary sub-group of Group II is further shown by the low solubilities of its carbonate and its phosphate (relation to lithium), but its very soluble sulphate, chromate, ferrocyanide, and iodate set it apart from the alkaline earths and rare earths.

In the group, calcium, strontium, and barium, there is but one salt of these elements, the fluoride, which links this group with the group of the alkalis. Like the normal fluorides of lithium, sodium, potassium, rubidium and cesium, the normal fluorides of calcium, strontium, and barium are isotropic and crystallize in cubes and octahedra, and they may thus be confused with the fluorides of the alkalis when HF is employed as a reagent.

Although the alkaline earths are very closely related one to another in their general properties the differences in the solubilities of their typical salts and the differences in the appearances of these salts on the object slide enable the analyst to differentiate readily between them. There is also little danger of confusing them with other members of Group II, though it is well to bear in mind that if the ions Ag^+ , Hg^+ , or Pb^{++} are present, crystalline compounds may be obtained when testing for the alkaline earths.

The element magnesium falls in a micro-analytical group by itself, save for its behavior with Na^+ and UO_2^{++} acetates. Unlike its near relatives zinc and cadmium, it does not form a difficultly soluble double thiocyanate with mercury, while its very soluble sulphate, chromate, ferrocyanide, oxalate, and tartrate set it apart from the alkaline earths, and its soluble iodide differentiates it from mercury. Its hydroxide is not soluble in NaOH or KOH.

Mercury also must be set apart by itself and made the object of special tests. Save when in the mercurous state, this element shows little in common with the other elements in Group II so far as microscopic qualitative analysis is concerned.

DETECTION OF CALCIUM, STRONTIUM, BARIUM

A—By Means of Dilute Sulphuric Acid — H_2SO_4 .

Compounds Formed — $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

SrSO_4

BaSO_4 .

Apply the reagent by Method I, page 30, to a cold, neutral (or very slightly acid) moderately concentrated test drop.



FIG. 52. Barium with Iodic Acid.
100X.

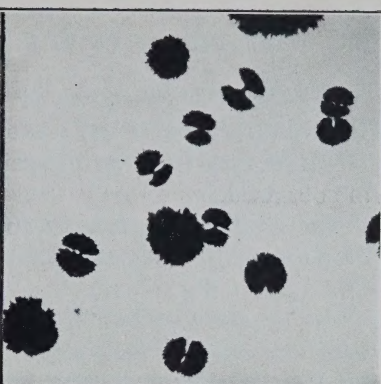


FIG. 53. Strontium with Iodic Acid.
100X.

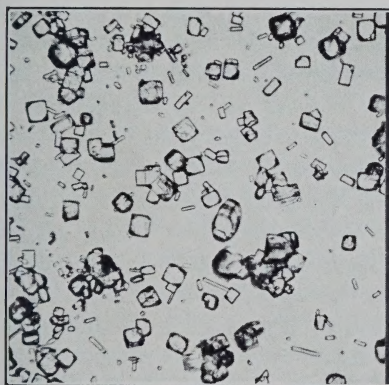


FIG. 54. Calcium with Potassium
Ferrocyanide. 800X.

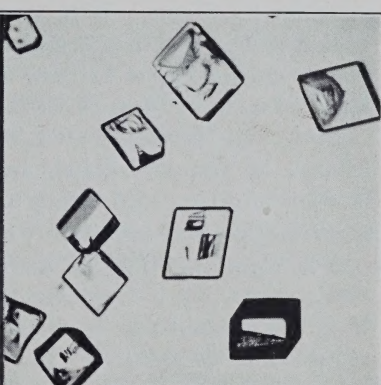


FIG. 55. Barium with Potassium
Ferrocyanide. 70X.

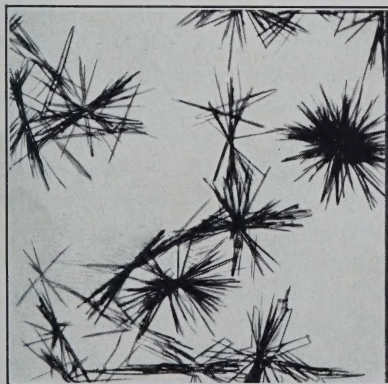


FIG. 56. Calcium with Sulphuric
Acid. 100X.

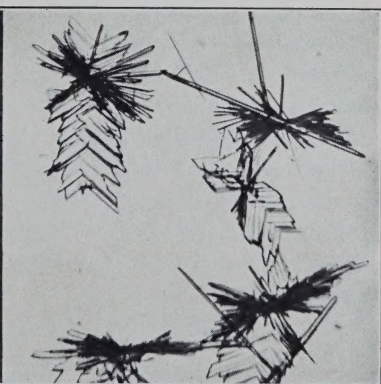


FIG. 57. Calcium with Sulphuric
Acid. 100X.

Free HCl or HNO_3 retard the separation of the crystals of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, but if the concentration of Ca^{++} is high, this retardation may be a distinct gain, for more characteristic crystals are obtained.

The first crystals usually appear at the periphery of the test drop nearest the reagent. They are long, slender, colorless needles, exhibiting oblique extinction (monoclinic) (Fig. 56, page 97). These needles first terminate in very slender points, but later as they develop into long narrow thin monoclinic prisms the ends become irregularly obliquely truncated (the acute angle is approximately 66° , a feature that is very characteristic of this salt). Needles and prisms occur singly, in sheaves, rosettes, X's and irregular fragments. With time the prisms broaden into masses of thin plates piled over one another like scales or shingles. These masses are built up of twins or fourlings. This change from acicular crystals to plates is characteristic of Ca^{++} (Fig. 57, page 97).

Bi^{+++} and Hg^+ may under certain conditions yield sheaves and rosettes of acicular crystals but in neither case do the needles develop into long thin prisms with obliquely truncated ends, and never do they give plates in twins and fourlings like $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

If no crystals of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ appear at first, set the preparation aside, examining it from time to time. This procedure is safer than heating to hasten evaporation or the addition of alcohol to reduce the solubility of the calcium sulphate. Moreover, if heated too high, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ passes over into CaSO_4 ,¹ thus introducing a crystallographic complication.

In solutions of concentrations such that the calcium salt is incompletely dissociated (that is, that Ca^{++} is in whole or in part present in a complex) the separation of the salt $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is more or less inhibited. Boron complexes are especially detrimental (Behrens). Boiling the "unknown" with concentrated HNO_3 will usually destroy the complex; but under these conditions all excess of HNO_3 must be driven off since $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is soluble in this acid. HNO_3 appears to give better results than treatment with HCl. Moreover, it has been shown that $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is not readily formed in the presence of much CaCl_2 .

Before deciding that calcium is absent, it is wise to test for the

¹ See Mellor: *Comprehensive Treat. Inorgan. and Theoret. Chem.* Vol. III, p. 779.

presence of NH_4 (*i.e.*, NH_3). Under certain conditions of concentration calcium sulphate is soluble in ammonium sulphate because of the formation of the double salt $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$. This double salt is decomposed by an excess of water, with reprecipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, but no dependence should be placed upon this probable reprecipitation in microscopic qualitative analysis.

Most salts of the trivalent metals interfere more or less seriously with the sulphate test for calcium. Under these conditions, it is best to precipitate the alkaline earths with ammonium oxalate in neutral concentrated solution, separate and wash (once) the precipitate by means of the centrifuge. Then test the precipitate with H_2SO_4 as suggested above.

Strontium yields a granular crystalline precipitate. Sometimes if viewed immediately after the inflow of the reagent, sheaves and masses of very tiny acicular crystals of SrSO_4 are seen, but these rapidly disintegrate into a granular deposit in which even a high power fails to reveal any distinctive features.

Because of its very low solubility and precipitation at room temperatures, BaSO_4 usually separates in so finely divided a condition as to appear to be amorphous under the magnifications applicable to uncovered drops in microscopic qualitative analysis. But digestion with HCl may yield crystals in the form of tablets.

Lead also forms a sulphate, PbSO_4 , of very low solubility, and is generally precipitated at once in a finely dispersed condition not distinguishable from BaSO_4 . In a short time, however, this fine precipitate becomes granular and is then indistinguishable from SrSO_4 ; still later crystallites and skeleton crystals may appear, the most characteristic form being X's with peculiar curved arms, and these in turn may develop into rhombic plates. Very rarely, the addition of H_2SO_4 causes the separation of well-formed orthorhombic prisms. PbSO_4 is soluble in NaOH and in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solutions, but the sulphates of the alkaline earths are not appreciably soluble in these reagents.

The sulphates of Hg^+ and Ag^+ are only slightly soluble in water and therefore will separate if present, but since they form moderately large prismatic crystals they cannot be mistaken for the alkaline earths. The same is true of Tl^+ . Bi^{+++} and Sb^{+++} may be precipitated as white basic salts.

A saturated solution of CaSO_4 gives no precipitate with salts

of Ca^{++} , but causes a slow separation of SrSO_4 and an immediate separation of BaSO_4 .

$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is converted into CaCO_3 by heating with $(\text{NH}_4)_2\text{CO}_3$ solution, and if heated with an alkali tartrate $\text{CaC}_4\text{H}_4\text{O}_6$ is formed.

Calcium selenate, $\text{CaSeO}_4 \cdot 2 \text{H}_2\text{O}$, is isomorphous with $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, but is more soluble than the latter and therefore unsuited for the detection of Ca^{++} .

It has been implied above that many compounds when in solution materially increase the solubility of calcium sulphate. If the solubility of calcium sulphate in water be taken as unity, the ratio increase in solubility in round numbers at 20° – 25° may be expressed thus:²

H_2SO_4	10×	CaNO_3	5×
H_3PO_4	20×	$\text{Mg}(\text{NO}_3)_2$	26×
NH_4Cl	20+×	$(\text{NH}_4)_2\text{SO}_4$	8×
Alkali halides	17–×	Alkali sulphates	4×
CaCl_2	5×	MgSO_4	7×
MgCl_2	26×	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	4×
NH_4NO_3	18×		

$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is readily soluble in HCl at room temperature; SrSO_4 is only slightly so, while BaSO_4 is practically insoluble. The granular precipitate of SrSO_4 is soluble in boiling HCl from which it separates on cooling in sheaves of acicular crystals, long thin prisms, short rods and square and rectangular plates. $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ separates from HCl solutions without change of habit. Although the crystals of SrSO_4 and $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ obtained by recrystallization from HCl usually differ in appearance, they may appear sufficiently alike to lead to doubt in the mind of the analyst. Recrystallization from HCl or HNO_3 is of very doubtful value as a means of distinguishing between Ca^{++} and Sr^{++} , but the varying solubilities of the sulphate compounds afford a means of separating the alkaline earths.

$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is 2000 times, and SrSO_4 40 times as soluble as BaSO_4 in water at room temperatures.³

² Calculated from data in Comey: *Dictionary of Solubilities*; Seidell: *Solubilities of Inorganic and Organic Compounds*.

³ Schoorl (quoting deKoninck): *Beiträge*, p. 113.

Identification of the Alkaline Earth Sulphates in Mixtures.

I—Calcium is absent. (See page 98.) — Evaporate the test drop to dryness so as to cause the granular or “amorphous” precipitate to cling to the object slide. Carefully cover the dry precipitate with water, warm *very gently*, decant and reject the wash water. Scrape the precipitate into a tiny compact mass, add thereto a *small* drop of concentrated H_2SO_4 . Heat until copious white fumes of SO_3 are evolved, being careful to hold the object slide tipped and to apply the heat of the micro-flame above the drop of acid in order to prevent the hot H_2SO_4 from creeping over the slide. As soon as it is evident that the bulk (or all) of the precipitate has passed into solution, remove from the flame, tip the slide so that all the acid collects at the corner of the slide and touch this drop of hot acid to the surface of a clean slide; a small moderately rounded, clear drop should be thus obtained. SrSO_4 or BaSO_4 have passed into solution owing to the formation of acid sulphates $\text{Sr}(\text{HSO}_4)_2$, $\text{Ba}(\text{HSO}_4)_2$. These acid sulphates are readily decomposed by water with the reprecipitation of the normal sulphates. If this decomposition is slow, the normal sulphates are given an opportunity to crystallize. Reprecipitation is effected by breathing gently upon the acid drop, once or twice, and allowing the preparation to stand at room temperature. In a few seconds crystals of the normal sulphates appear, at first about the circumference of the drop and later throughout its entire volume.

When recrystallized thus, SrSO_4 separates in the form of irregular granules, fusiform bodies, rhombic plates, and, most characteristic of all, spindle-shaped crystals swelling at the middle of their length so as to give the appearance of slender crosses with tapering arms; both of the cross-arms being very short, the crystals may appear dagger-shaped (Fig. 58, page 103).

BaSO_4 separates in very different crystal forms. Instead of the slender fusiform crystals and crosses with two short cross-arms, X-shaped skeletons with more or less feathery arms appear; usually two of the arms are much longer than the other two, and since the shorter are always on the same side, the crystals have somewhat the appearance of a distant view of a flying bird. These X's grow quite large and are constant and peculiar to Ba^{++} . When the X's are small and are cross-like the arms are nearly symmetrical but cannot be confused with the crosses of fusiform crystals of SrSO_4 . Fig. 59, page 103.

Mixtures of SrSO_4 and BaSO_4 may occasionally yield typical crystals of both SrSO_4 and BaSO_4 , but usually the mixed, reprecipitated, sulphate possesses the characteristics of neither element.

PbSO_4 , when dissolved in concentrated H_2SO_4 and reprecipitated as above described, separates first in forms closely simulating SrSO_4 (Fig. 103, page 169) and later the skeleton crystals may become feathery and resemble BaSO_4 . If a fragment of KI is added, PbI_2 is formed. (See Pb, page 180.)

In order to obtain characteristic crystals of SrSO_4 , BaSO_4 , or PbSO_4 the H_2SO_4 used must be pure. Acid which has stood in small reagent bottles for a long time usually dissolves sufficient material from the glass to prevent the formation of characteristic crystals.

SrSO_4 can be recrystallized by boiling with strong HCl, in which BaSO_4 is practically insoluble. On cooling there will separate, square and rectangular plates, long thin prisms, sheaves of acicular crystals and short rods. The crystals obtained from HCl solutions are not as characteristic as those from hot concentrated H_2SO_4 , and are valuable only as a means of distinguishing between strontium and barium, but lead must be absent.

II—Calcium is found to be present by the formation of the sheaves and bundles of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. This salt can be recrystallized from hot concentrated H_2SO_4 as described above, but the reprecipitated salts CaSO_4 , or $\text{Ca}(\text{HSO}_4)_2$ or a mixture of the two are not sufficiently characteristic in appearance to serve in microscopic qualitative analysis. Usually somewhat oval granular plates first appear; these in a short time "sprout" at the ends and grow into tufts of tiny needles or curving dendritic masses.

Calcium seriously interferes with the detection of strontium and barium if the recrystallization method is employed.

Before treating the precipitated sulphates with H_2SO_4 , the CaSO_4 should be removed by one of the following methods:

1—Extract repeatedly with distilled water at not over 25°C . If the temperature is raised $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ passes over into CaSO_4 , whose solubility decreases with a rise in temperature.

2—Extract the sulphates with dilute HNO_3 (0.1 N) at room temperature. $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ is readily soluble; SrSO_4 only slightly soluble; BaSO_4 is almost insoluble.

3—Boil the sulphates with a solution of $\text{NaKC}_4\text{H}_4\text{O}_6$. Calcium

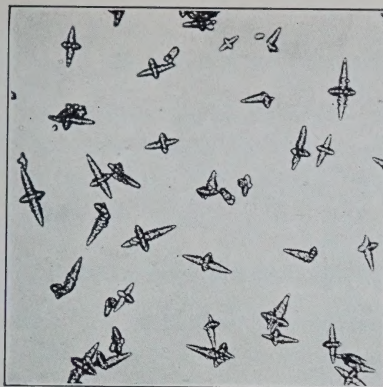


FIG. 58. Strontium Sulphate Recrystallized from Conc. Sulphuric Acid. 200 $\times$.



FIG. 59. Barium Sulphate Recrystallized from Conc. Sulphuric Acid. 200 $\times$.

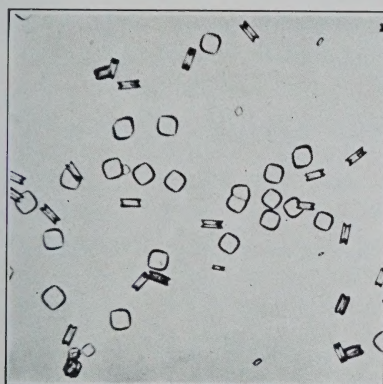


FIG. 60. Calcium with Oxalic Acid. 400 $\times$.

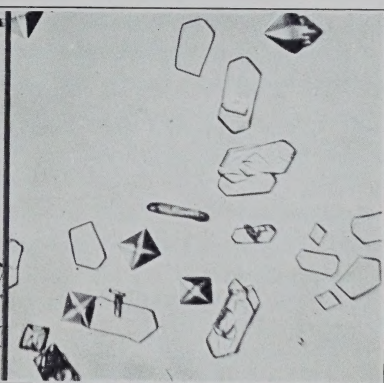


FIG. 61. Strontium with Oxalic Acid. 250 $\times$.

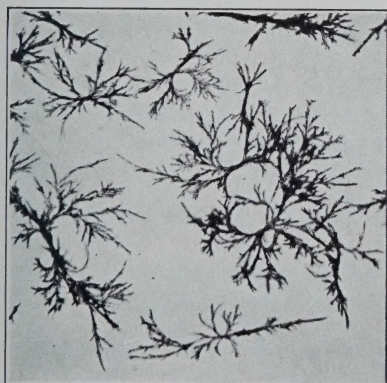


FIG. 62. Barium with Oxalic Acid. 100 $\times$.

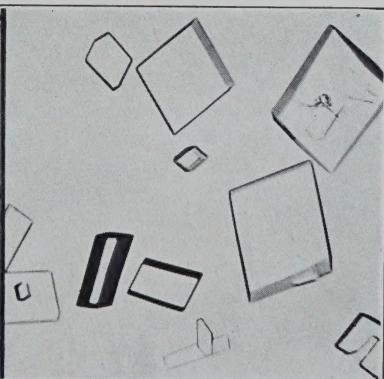


FIG. 63. Beryllium with Potassium Oxalate. 100 $\times$.

sulphate alone is converted into tartrate. $\text{CaC}_4\text{H}_4\text{O}_6$ is readily soluble in dilute HCl . Decant and wash the precipitate.

4—Boil the sulphates with a concentrated solution of $(\text{NH}_4)_2\text{CO}_3$. Calcium and strontium are converted into carbonates but BaSO_4 remains unchanged.

5—Boil the sulphates with HCl . (See Calcium, page 100.)

III—Lead is present— This is ascertained by testing for lead in the original material or by adding KI to a portion of the sulphates. PbI_2 is formed.

1—Extract the PbSO_4 by heating with a concentrated solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in which PbSO_4 is soluble.

2—Extract with a moderately concentrated solution of NaOH , in which PbSO_4 is soluble; but unless the concentrations are just right a hydrated oxide of lead may be formed which does not entirely pass into solution.

IV—After removing Ca^{++} and Sr^{++} recrystallize the residue of BaSO_4 by heating with H_2SO_4 .

Experiments.

(a) — Precipitate CaSO_4 by means of dilute H_2SO_4 , from a salt of calcium in neutral solution.

(b) — Try the effect of precipitating in the presence of free HCl ; then in the presence of free HNO_3 .

(c) — Precipitate with dilute H_2SO_4 , then heat, adding more acid if necessary, until white fumes are given off; cool, breathe on the preparation and examine.

(d) — Try testing for a trace of Ca in the presence of a large quantity of salts of the elements of Group I. A retardation of the reaction results.

(e) — Try effect of a solution of $(\text{NH}_4)_2\text{CO}_3$ on crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

(f) — To a drop of moderately dilute solution of SrCl_2 , add dilute H_2SO_4 and examine at once.

(g) — Recrystallize SrSO_4 from H_2SO_4 and from HCl .

(h) — Make a mixture of Ca and Sr salts and add H_2SO_4 . Recrystallize the product from H_2SO_4 without having removed the Ca . In another portion remove the Ca by extracting with boiling water and then recrystallize the residue.

(i) — Precipitate BaSO_4 by means of dilute H_2SO_4 , from a very dilute solution of a barium salt.

(j) — Make a mixture of salts of Ca and Ba , recrystallize at once without removing the Ca . From another portion remove the Ca with hot water and recrystallize the residue.

(k) — Try a mixture of Sr and Ba . Remove the Sr by treating with HCl and recrystallize the residue.

(l) — Try a mixture of Ca, Sr and Ba, recrystallizing at once, then removing in turn the Ca with hot water and the Sr with HCl.

(m) — After having tried the other reactions for Ba, fuse some BaSO_4 with K_2CO_3 and proceed as directed above.

B—By Means of Oxalic Acid — $\text{H}_2(\text{C}_2\text{O}_4) \cdot 2 \text{H}_2\text{O}$.

Compounds Formed — $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$

$\text{Sr}(\text{C}_2\text{O}_4) \cdot n \text{H}_2\text{O}$

$\text{Ba}(\text{C}_2\text{O}_4) \cdot n \text{H}_2\text{O}$.

Apply the reagent, at room temperature, by Method I, page 30, to a neutral solution or to one slightly acidulated with acetic acid.

Under these conditions, the calcium salt obtained will be $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$ in the form of tiny highly refractive, strongly birefringent tetragonal octahedra, rhombs, drusy crosses, rectangular plates or tablets which are almost square (Fig. 60, page 103). From hot solutions or those containing a small amount of free mineral acid the monoclinic salt $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ may separate; this monohydrated oxalate has little value in microscopic qualitative analysis since its habit is such as to render very difficult its differentiation from the oxalates of many other elements.

$\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$ is only slightly soluble in solutions containing acetic acid, alkali acetates or ammonium hydroxide, but is very soluble in dilute mineral acids. Hence before testing for the alkaline earths with oxalic acid, it is wise to add sodium or ammonium acetate to the test drop. A trace of free HNO_3 is sometimes desirable, however, when only Ca^{++} salts are present and their concentration high, for the separation of $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$ is retarded and larger and more easily recognized crystals are obtained.

The oxalate test should always be confirmed by the sulphate test. The mother liquor is decanted from the precipitated oxalates, or recourse may be had to filtration or to the centrifuge. Wash at least once with distilled water. Scrape together the precipitate and cover with a moderate-sized drop of dilute H_2SO_4 ; calcium oxalate will be dissolved and in a few minutes characteristic crystals of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ will be obtained if calcium is present.

Strontium gives with oxalic acid $\text{SrC}_2\text{O}_4 \cdot n \text{H}_2\text{O}$, in either tetragonal or monoclinic crystals depending upon temperature conditions. At room temperature the tetragonal form may be expected. This salt separates in "octahedra," and in symmetrical crosses

with pointed arms bounded by curves; the latter are skeleton crystals and are forms rarely obtained with calcium oxalate. On long standing, six-sided plates or square and rectangular, short, stout bipyramidal prisms appear (Fig. 61, page 103). Usually the oxalate crystals formed by strontium are not readily distinguished from the corresponding oxalates of calcium save that they are apt to be larger and better developed. In mixtures the two oxalates are indistinguishable; recourse may then be had to the H_2SO_4 treatment described above.

Barium also forms with $\text{H}_2\text{C}_2\text{O}_4$ several oxalates $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. At room temperature the crystals separating are very different from those obtained with calcium or strontium; large branching aggregates in fibrous bundles or sheaf-like masses of fibrous drusy dendrites are obtained (Fig. 62, page 103). Not infrequently small monoclinic prisms are also formed, but the latter are in no way characteristic. $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ is soluble in $\text{HC}_2\text{H}_3\text{O}_2$, readily so if heated, and is so soluble in HNO_3 that a bare trace of this acid will prevent the separation of $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ in the test drop.

If calcium or (and) strontium are present the characteristic aggregates of the barium salt will not be obtained. Recourse may then be had to precipitation of the calcium and strontium oxalates in the presence of very dilute HNO_3 ; after an interval of a few minutes the oxalates of calcium and strontium will have separated; the mother liquor is then decanted and to it is added a fragment or two of $\text{NaC}_2\text{H}_3\text{O}_2$ to mitigate the solvent action of the HNO_3 ; usually barium oxalate will then separate in the form of rosettes of thin prisms; this reaction is not reliable when dealing with complex mixtures, especially as magnesium may mask the reaction.

From hot solutions $\text{BaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ separates in strongly birefringent orthorhombic plates and tabular crystals.

Although Fe^{+++} and Al^{+++} have no appreciable influence upon the oxalate reaction for Ca^{++} and Sr^{++} they completely change that obtained with Ba^{++} because of the formation of a double salt (?) which separates in very long hair-like crystals (trichites) both straight and curved; the phenomenon is very characteristic. With Fe^{+++} the tufts are brown, with Al^{+++} colorless (brownish if very fine [structural color]). H_2PtCl_6 induces the formation of less striking trichites.⁴

⁴ A similar formation of trichiten crystals takes place when calcium is precipitated as oxalate in the presence of palladium chloride in acid solutions.

The presence of acetic acid facilitates the separation of typical crystals of calcium oxalate, retards the separation of strontium oxalate, and may entirely inhibit the separation of barium oxalate.

The oxalates of all three alkaline earths are readily soluble in dilute HCl and in dilute HNO_3 , but are reprecipitated by NH_4OH . All three are converted into sulphates by dilute H_2SO_4 .

Magnesium oxalate separates from solutions strongly acidulated with $\text{HC}_2\text{H}_3\text{O}_2$ in forms that are indistinguishable from those of calcium oxalate. If in doubt, decant, wash the oxalate crystals, dissolve in dilute HCl or HNO_3 and add NH_4OH in excess. The oxalates of the alkaline earths will be reprecipitated, but the oxalate of magnesium will not. Magnesium oxalate is not precipitated if ammonium salts are present.

Ag^+ , Cu^+ , Be^{++} , Zn^{++} , Cd^{++} , Pb^{++} , Sn^{++} , Sn^{++++} , Sb^{+++} , Bi^{+++} , Mn^{++} , and the rare earths may each and all, under certain conditions, yield crystals so closely resembling the oxalates of Ca^{++} and Sr^{++} as to render it a difficult task to distinguish between them without having recourse to determination of their optical constants.

Oxalic acid must, therefore, be regarded as a reagent whose chief usefulness is that of merely indicating the presence or absence of a number of elements. It is rare indeed that it can be employed for positive identification.⁵

In the presence of alkali oxalates, double oxalates may be formed of sufficiently low solubility as to bring about a separation of more or less well-formed crystals in the test drop. The elements which most often give rise to the separation of double oxalate crystals are: thallium, uranium, manganese, antimony, bismuth, iron, nickel, cobalt, and palladium.

In spite of its obvious limitations, precipitation of the alkaline earths as oxalates has its advantages, for it serves to indicate the presence of calcium, strontium, and barium in mixtures containing trivalent metals, borates, and many complexes where other reagents sometimes fail to yield a satisfactory crystalline precipitate.

A most curious anomaly in the habits of the alkaline earth oxa-

Instead of the tiny tetragonal octahedra of the salt $\text{CaC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$, long hair-like crystals with tufted ends are obtained. In the presence of palladium, strontium behaves similarly, but barium yields rods only, no trichites.

⁵ See in this connection Whitmore and Schneider: *Mikrochemie* 7, 295 (1930).

lates when formed in the presence of stannic chloride (chlorostannic acid) was pointed out by Behrens many years ago. Although we know of no other compound similarly affecting the crystallization of these oxalates, it is reasonable to suppose that others exerting a similar action probably exist. So striking and characteristic is the change in habit produced by H_2SnCl_6 that this can be employed to distinguish between calcium, strontium, and barium.

This modified test can be performed as follows. To the neutral moderately concentrated test drop add a very little H_2SnCl_6 ; stir thoroughly. At the center of the drop thus prepared add a fragment of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$. In a few seconds instead of the usual oxalate crystals there will be seen, if calcium is present, tiny rounded grains and thin disks. Some of the grains show evidences of being octahedra with rounded edges and rounded angles. They are smaller than $\text{CaC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ crystals obtained with pure calcium salts. Strontium forms at once *large*, brilliant, well-developed tetragonal octahedra, but these beautiful crystals soon become corroded, crumble into fine powder and gradually disappear. Instead of its usual branching forms barium gives clean-cut rectangular prisms terminating in pyramids, prisms tapering to a point, and masses of prisms with obliquely truncated ends. If much barium is present, long, very pointed, fusiform crystals, singly or in radiating masses, or bundles of very slender pointed needles, are obtained.

The solubilities of the oxalates of calcium, strontium, and barium in water at room temperature are not direct functions of the atomic weights of the elements. The calcium salt is the least soluble of the three and the strontium salt the most soluble.

Zinc yields $\text{ZnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ in tiny pseudo-octahedra usually united in twos, or double spherulites resembling dumb-bells, but thin rhombs or short stout rods with rounded ends are sometimes formed. Few crystals of zinc oxalate show distinct angles. When single octahedra are obtained their resemblance to calcium and to strontium oxalates is such as to lead to confusion. The oxalate test for zinc is unreliable in mixtures (Fig. 64, page 109).

Cadmium gives long, thin, colorless monoclinic prisms with obliquely truncated ends; singly, in X's, or in irregularly radiating groups (Fig. 65, page 109). This salt has the formula $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$, but from concentrated solutions well-formed octahedra separate that are not distinguishable from the oxalates of zinc,

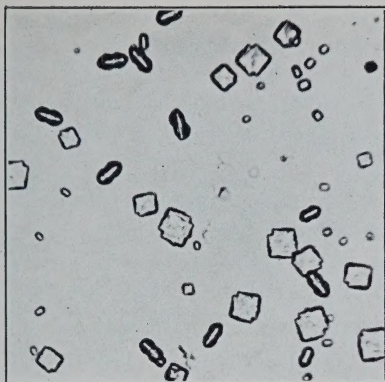


FIG. 64. Zinc with Oxalic Acid.
300 $\times$.

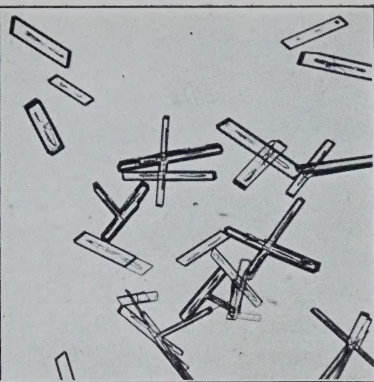


FIG. 65. Cadmium with Oxalic Acid.
100 $\times$.

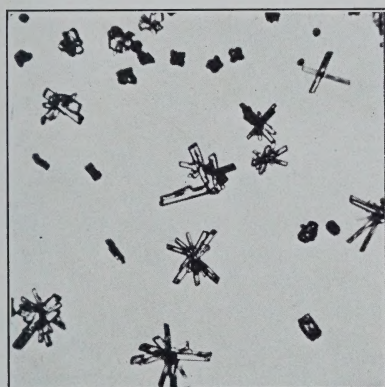


FIG. 66. Bismuth with Potassium
Oxalate. 200 $\times$.

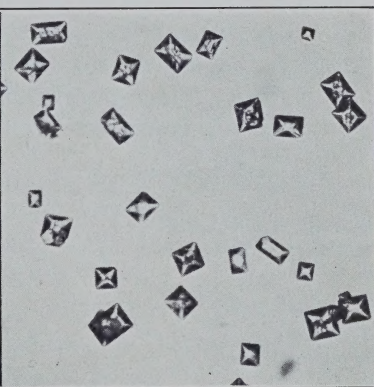


FIG. 67. Bismuth with Potassium
Oxalate. 400 $\times$.

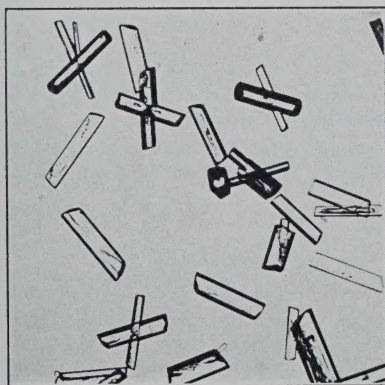


FIG. 68. Tin (Sn^{++}) with Potassium
Oxalate. 100 $\times$.

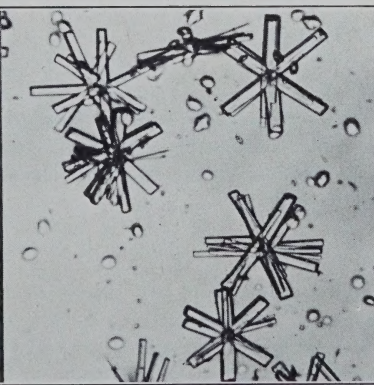


FIG. 69. Manganese (Mn^{++}) with
Potassium Oxalate. 100 $\times$.

calcium, or strontium. The presence of calcium, strontium, or zinc prevents the formation of the prismatic type of cadmium oxalate.

Manganous salts form $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ in long slender prisms or six-armed star-like groups; the latter result from the intersection of twinned prisms (Fig. 69, page 109). Manganous oxalate is strongly birefringent with parallel extinction. The best crystals are obtained when the dilute test drop is acidified with acetic acid. Free mineral acids must be absent. Good results are obtainable only when manganous salts are present in considerable excess compared with the salts of other elements precipitable by oxalic acid.⁶

Since oxalic acid (or an acid alkali oxalate) gives a precipitate with a large number of elements it is essential that the analyst confirm his findings by several other tests. Errors are less liable to be made if the analyst consults the following table of oxalates most frequently precipitated.

<i>The precipitate consists of:</i>	<i>Possible presence of the elements grouped below:</i>
Granules or is pulverulent "Octahedral" crystals	Ag; Pb; Bi; Rare Earths; Ni; Hg Ca; Sr; (Ba); Zn; Cd; Zr; Mg; Pb; Mn; Bi
Spherulites or disks	Ag; Zn; Cd
Trichites	Ba with Fe or Al; Ca or Sr with Pd
Dendritic masses	Pb; Sn; Hg; Ba
Prisms, plates	Ag; Ti^+ ; (Be); Zn; Cd; Pb^{++} ; Sn^{++} , Fe^{++} , Mn^{++} ; U; Bi
Slender prisms, fine needles or rods, singly or in groups or radiates	(Be); Cd; Pb^{++} ; Sb; Bi; Rare Earths; Mn^{++} ; Rh; Pd; Hg; Ba

Experiments.

(a) — Try the reaction with oxalic acid after the manner given above, on a salt of Ca in a neutral solution. Try again in the presence of a strong acid.

(b) — Precipitate $\text{CaC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$, draw off the supernatant liquor, and treat the residue with dilute H_2SO_4 . After examining the preparation, add more acid, and heat until white fumes appear; cool; breathe upon the preparation and examine again.

(c) — Test a drop of SrCl_2 solution with $\text{H}_2\text{C}_2\text{O}_4$.

(d) — Treat the oxalate thus obtained with H_2SO_4 and recrystallize.

⁶ Both mercurous and mercuric salts are precipitated as oxalates of low solubility; the character of the precipitates varies with concentration, temperature, and acidity of solution, but it should not be forgotten that oxalic acid gives no precipitate with solutions of mercuric chloride or bromide.

- (e) — Test a salt of Ba with $\text{H}_2\text{C}_2\text{O}_4$, in both hot and cold solutions.
- (f) — Make a mixture of Ca, Sr, Ba. Add $\text{H}_2\text{C}_2\text{O}_4$. Repeat the experiment in HNO_3 solution; after a few minutes, decant the clear solution, concentrate slightly and add $\text{NaC}_2\text{H}_3\text{O}_2$.
- (g) — Try the effect of the presence of FeCl_3 on the precipitation of oxalates of Ca, Sr, Ba; first each element separately, then in mixtures of Ca and Ba; Sr and Ba; Ca, Sr and Ba.
- (h) — Try $\text{H}_2\text{C}_2\text{O}_4$ on a salt of Mg, then add an excess of $\text{HC}_2\text{H}_3\text{O}_2$ to the test drop and examine again.
- (i) — Test salts of Zn, Cd, Bi, Pb and Ag.
- (j) — To a test drop containing Ca and SnCl_2 add oxalic acid. Compare the oxalate obtained with Ca oxalate formed in the absence of SnCl_2 .
- (k) — Repeat the experiment with a salt of Sr. With a salt of Ba.

C—By Means of Sodium Tartrate Strongly Acidified with Tartaric Acid — $\text{HNaC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O} + \text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

Compounds Formed — $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$
 $\text{Sr}(\text{C}_4\text{H}_4\text{O}_6) \cdot n \text{H}_2\text{O}$
 $\text{Ba}(\text{C}_4\text{H}_4\text{O}_6) \cdot n \text{H}_2\text{O}$.

The reagent may be applied by Method III as suggested under Potassium, page 72, but better-formed crystals of calcium tartrate are obtained if the reagent is added by Method I, page 30.

The test drop should be moderately concentrated with respect to Ca^{++} , and should be acidified with $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$, but free mineral acids must be absent, since $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$ is readily soluble in these acids. To guard against their inhibitory effects a tiny fragment of $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3 \text{H}_2\text{O}$ may be added as a routine procedure.

$\text{Ca}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4 \text{H}_2\text{O}$ separates slowly in the form of large, colorless, brilliant, strongly birefringent orthorhombic prisms, with obliquely truncated ends (Fig. 70, page 113), singly, in clusters, and in masses. Characteristic penetration twins are frequent.

In dilute solutions the crystals appear only after a long time, while on the other hand, if the test drop is too concentrated, non-characteristic prisms and crystallites are precipitated.

Strontium forms a similar compound, isomorphous with the calcium salt and not readily distinguishable from it, even though it has a tendency to form shorter, stouter prisms.

Barium yields an immediate precipitate in the form of a very fine powder.

Lead tartrate is first precipitated in a fine granular condition. Soon, however, irregular bristly masses and crystallites are formed,

whose appearance is quite different from the tartrates of calcium and strontium.

Much magnesium seriously interferes with the formation of typical tartrates of calcium and strontium and their habit may be greatly modified.⁷

The appearance and properties of the tartrates of the alkali metals have already been discussed on pages 72-74.

Calcium sulphate heated in a solution of alkali tartrate is converted into calcium tartrate which is readily soluble in dilute HCl. This reaction can be turned to advantage when dealing with a mixture of the sulphates of calcium, strontium, and barium, for the sulphates of strontium and barium are unaffected by heating with sodium tartrate or with sodium potassium tartrate.

Testing complex mixtures for calcium by the tartrate method is of little value, since well-formed characteristic crystals are obtainable with comparatively pure salts of calcium only, but with salts of calcium in the absence of strontium, barium, lead, and thallium the reaction is characteristic and leaves little to be desired. The formation of calcium tartrate constitutes a valuable reaction for the identification of tartaric acid.

Experiments.

- (a) — Test a salt of Ca.
- (b) — Repeat, having a strong acid present. Then repeat, having $\text{NH}_4\text{-C}_2\text{H}_3\text{O}_2$ present.
- (c) — Test salts of Sr and Ba.
- (d) — Test a mixture of Ca and K.

D-By Means of Ammonium Carbonate — $(\text{NH}_4)_2\text{CO}_3$.

Compounds Formed — CaCO_3

SrCO_3

BaCO_3 .

To a moderately concentrated solution of the material to be tested, neutral if possible, or at the most only very slightly acid, add one or more fragments of "ammonium carbonate"⁸ (Method II, page 32.) *Warm gently*, but avoid boiling. An excess of the reagent and avoiding boiling is essential since otherwise the re-

⁷ See Behrens-Kley: *Mikrochemische Analyse*, p. 52.

⁸ This reagent as ordinarily encountered consists of a mixture of carbonate, bicarbonate, and carbamate. Carbamates of the alkaline earths are soluble, but unstable and converted into carbonates on heating.

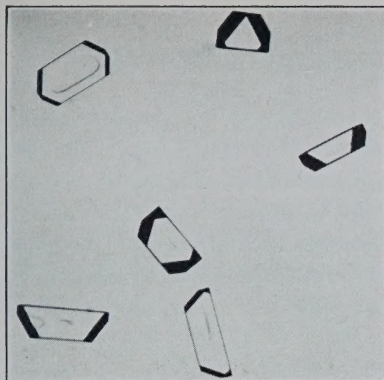


FIG. 70. Calcium with Sodium Tartrate. 100 $\times$.

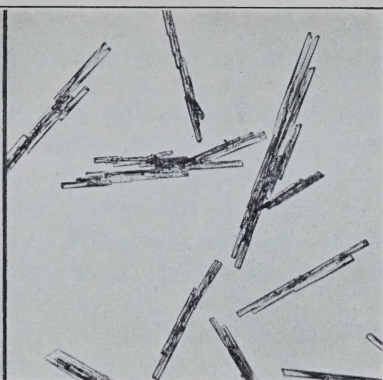


FIG. 71. Calcium with Arsenic Acid. 50 $\times$.

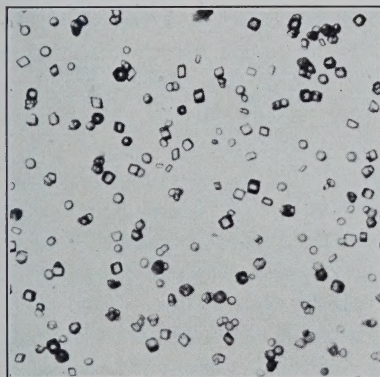


FIG. 72. Calcium with Ammonium Carbonate. 500 $\times$.

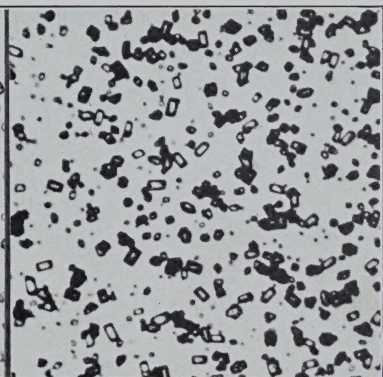


FIG. 73. Barium with Potassium Chromate. 500 $\times$.

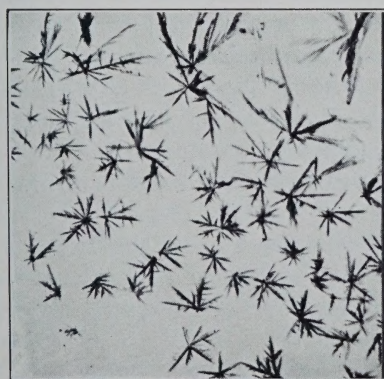


FIG. 74. Magnesium with Disodium Phosphate and Ammonium Hydroxide. 50 $\times$.



FIG. 75. Magnesium with Disodium Phosphate and Ammonium Hydroxide. 100 $\times$.

action is a reversible one. The reaction is slow; the precipitate first formed is "amorphous" and only becomes crystalline on standing (Fig. 72, page 113). Of the three alkaline earth carbonates formed in this manner, that of barium is least soluble, and that of calcium most soluble. All three are dimorphic; the crystals are either hexagonal or orthorhombic, according to conditions. If the temperature has not been too high, hexagonal forms should be obtained in the test.

Calcium gives tiny disks and well-defined rhombohedra; strontium, spherulites and dumb-bell aggregates of tiny needles, while barium maintains an "amorphous" form for a relatively long period and only partially changes to minute needles, spider-like aggregates, and tiny spherulites; the latter sometimes develop into spindles and dumb-bell masses. Strontium and barium carbonates are generally indistinguishable. All three carbonates are strongly birefringent. It is obvious that only in the case of calcium are characteristic crystals obtained.

$(\text{NH}_4)_2\text{CO}_3$ gives flocculent or granular precipitates with a large number of elements, hence this test is of little value in complex mixtures, but since the alkaline earth carbonates generally cling tightly to the object slide, precipitation with $(\text{NH}_4)_2\text{CO}_3$ may be a valuable means for group separations, for decantation is easily performed and the precipitate clinging to the slide may then be washed, and dissolved in acetic acid for the application of identity tests.

The reaction of $(\text{NH}_4)_2\text{CO}_3$ with lithium has already been described on page 89.

HNaCO_3 and HKCO_3 give reactions similar to $(\text{NH}_4)_2\text{CO}_3$, but when in large excess and heated at or near the boiling point double salts are formed, which in the case of calcium afford characteristic reactions. The formation of the salt $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5 \text{H}_2\text{O}$ has been suggested for the detection of calcium in simple mixtures, in plant juices, and in vegetable and animal tissues.

HNaCO_3 in excess yields a characteristic test for Zinc. (See page 132.)

Na_2CO_3 produces "amorphous" precipitates that in the case of strontium and barium retain their non-crystalline appearance on standing. Calcium carbonate slowly becomes crystalline if neither strontium nor barium is present.⁹

⁹ Molisch: *Ber.* **34**, 288, 357 (1916), suggests Na_2CO_3 or K_2CO_3 as exceptionally sensitive reagents for the demonstration of Ca^{++} in plant tissues, no matter in what form the Ca^{++} may be combined.

Hexagonal CaCO_3 (calcite) is isomorphous with hexagonal MgCO_3 , FeCO_3 , MnCO_3 , CoCO_3 , ZnCO_3 , and the solid solution of these carbonates with calcium carbonate. CaCO_3 is also theoretically isomorphous with hexagonal NaNO_3 .

Orthorhombic CaCO_3 (aragonite) is isomorphous with orthorhombic SrCO_3 , BaCO_3 and PbCO_3 and also with orthorhombic KNO_3 .

Hexagonal CaCO_3 — calcite — is the stable form, and orthorhombic CaCO_3 — aragonite — the metastable, but if even only very little SrCO_3 or PbCO_3 is present aragonite is stabilized (Mellor).

In view of these isomorphous series, it is evident that the alkaline earth carbonates will carry down with them other elements which may complicate an analysis.

Experiments.

(a) — Test in turn a calcium, a strontium, and a barium salt, with $(\text{NH}_4)_2\text{CO}_3$, using very dilute solutions.

(b) — Decant the mother liquor from the precipitated carbonates, and cover the residue with dilute H_2SO_4 . Note the conversion to sulphates.

E-By Means of Ammonium Bichromate — $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

Compounds Formed — SrCrO_4

BaCrO_4 .

Apply the reagent by Method II, page 32, to an acetic acid solution test drop. Only Ba^{++} will be precipitated at once in the form of tiny yellow grains and globular masses, short thick rods arranged in crosses and X's or rarely in rectangular plates; but all are so minute as to require a high power to resolve the crystals into more than irregular grains (Fig. 73, page 113).

When applying this test, be sure the test drop is dilute with respect to the alkaline earths. Do not stir the preparation after the fragment of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ has been introduced and avoid rubbing the glass with a glass rod or platinum wire. Rubbing causes an instantaneous precipitation of BaCrO_4 in so finely divided a condition as to render it amorphous in appearance. Moreover, other chromates are more likely to be precipitated, especially if the test drop is moderately concentrated. Allow to stand for some time to insure the separation of as much BaCrO_4 as possible.

Chromates of Ag^+ , Pb^{++} , Hg^+ , Hg^{++} , Tl^+ , and certain organic bases are also precipitated in acetic acid solutions and these inorganic cations also yield a precipitate in solutions acidified with

HNO_3 , whereas BaCrO_4 is soluble in HNO_3 and in HCl . Differentiation of simple salts is thus possible, but in mixtures separations are necessary before identification tests are applied.

Carefully decant the mother liquor. Into the decanted clear drop cause a drop of NH_4OH to flow; SrCrO_4 will be precipitated in tiny yellow globulites or dumb-bell shaped aggregates; short stout fusiform bodies are also formed. If the original acetic acid test drop is sufficiently dilute no precipitate should be produced if only Sr^{++} and Ca^{++} are present. Ca^{++} gives no precipitate in either neutral, acid, or alkaline solutions.

$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (or $\text{K}_2\text{Cr}_2\text{O}_7$) is used as reagent rather than K_2CrO_4 because the latter reagent may precipitate SrCrO_4 even in dilute acetic acid solution in forms not distinguishable from those of BaCrO_4 , save that the crystals are often much larger. Bichromates thus afford a convenient separation of Ca^{++} , Sr^{++} and Ba^{++} .

After SrCrO_4 has been precipitated by the addition of NH_4OH , decantation can again be practiced and to the decanted solution H_2SO_4 or $(\text{NH}_4)_2\text{C}_2\text{O}_4$ added to test for the presence of calcium.

Experiments.

- (a) — Try the bichromate reaction on salts of Ba, Sr, and Ca.
- (b) — Try mixtures of Ca and Ba, Sr, and Ba; use solutions acidified with $\text{HC}_2\text{H}_3\text{O}_2$, decant the clear solution, and to it add NH_4OH .
- (c) — Try the reagent upon Ba and Sr salts in HNO_3 solution. Then try it upon Ag, Pb, and mercurous salts in HNO_3 solution.

F—By Means of Potassium Ferrocyanide — $\text{K}_4\text{Fe}(\text{CN})_6$.

Compounds Formed — $\text{K}_2\text{CaFe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$

$\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 5 \text{H}_2\text{O}$.

Apply the reagent by Method I, page 30, to a moderately concentrated test drop which has been acidified with $\text{HC}_2\text{H}_3\text{O}_2$ and to which a very little NH_4Cl has been added.

Free mineral acids must be absent; it is therefore advisable always to add a little $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ to the test drop.

Calcium yields, almost immediately, tiny, practically colorless tetragonal crystals of the compound $\text{K}_2\text{CaFe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$ in the form of square and rectangular plates, many of them with beveled corners (Fig. 54, page 97). If the concentration is too high with respect to Ca^{++} a granular precipitate is formed, and if much NH_4Cl is present a very insoluble triple salt may be precipitated.

This salt is believed to have the formula $K_2CaFe(CN)_6 \cdot 4 (NH_4)_2CaFe(CN)_6$,¹⁰ and separates in a pulverulent form only.

Strontium gives no reaction save in very concentrated solutions, and then only as a fine granular deposit.

Barium forms large faintly yellow crystals of the moderately soluble orthorhombic salt $K_2BaFe(CN)_6 \cdot 5 H_2O$ of characteristic habit, in clear, transparent rhombs and rhombic tablets; the smaller equilateral rhombs give symmetrical extinction (Fig. 55, page 97). A triclinic modification $K_2BaFe(CN)_6 \cdot 3 H_2O$ is also known and may separate in the test drop if conditions are favorable for the formation of the unstable form.

The reagent $K_4Fe(CN)_6 \cdot 3 H_2O$ forms monoclinic crystals which under certain conditions may lead to confusion with the Ba^{++} double salt, if the test drop is allowed to evaporate until the concentration is such that the reagent begins to crystallize out.

If the test drop is alkaline, a magnesium ferrocyanide may be precipitated, which closely resembles the calcium salt, but no separation takes place in acid solutions nor in solutions containing moderate quantities of ammonium salts.

$K_4Fe(CN)_6$ precipitates many other elements as well as calcium and barium; most of these precipitates are heavy, voluminous, and non-crystalline; in this list of insoluble or very difficultly soluble ferrocyanides, the most frequently met with are lead, zinc, iron, copper, mercury, uranium, titanium, gallium, and some of the rare earths; of these the ferrocyanides of copper and uranium are brown; those of iron, blue.

Experiments.

(a) — Crystallize a little of the reagent $K_4Fe(CN)_6$, alone, and determine its optical properties.

(b) — Try the test on pure salts of Ca, Sr, Ba, using both dilute and concentrated solutions.

(c) — Try the reagent on mixtures of Ca and Sr, Ca and Ba, Sr and Ba.

(d) — Try the effect of the reagent on salts of Pb, Zn and Fe. Then make mixtures of Ba and these elements and test.

G-By Means of Arsenic Acid — H_3AsO_4 .

Compounds Formed — $NH_4CaAsO_4 \cdot 6 H_2O$.

To the drop to be tested, add sufficient NH_4OH to make it

¹⁰ Schoorl: *Beiträge z. Mikrochem. Anal.* p. 122.

Flanders: *Jour. Amer. Chem. Soc.* **28**, 1510 (1906).

Dains: *ibid.* **29**, 727 (1907).

neutral or very slightly alkaline. Cause to flow in (Method I, page 30) an ammoniacal solution of ortho-arsenic acid. A heavy granular precipitate is at once formed.

If barium is present, the precipitate remains granular; no crystals develop therefrom.

If strontium is present the granular deposit soon changes into minute stars and tiny disks.

But in the case of calcium, very large colorless skeleton crystals of the salt $\text{NH}_4\text{CaAsO}_4 \cdot 6 \text{H}_2\text{O}$ soon appear (Fig. 71, page 113). These crystals take the shape of elongated somewhat distorted X's; in time they fill out and simulate envelopes or even grow into prisms of the orthorhombic system, with faces reminding one of the roofs of houses. The forms assumed are identical with those of $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ described on page 77, but the skeletal crystals are usually larger and the prisms less abundant. (See Fig. 75, page 113).

Since most arsenates and phosphates of similar elements are isomorphous, it is to be expected that those cations which yield crystalline simple or double phosphates will also yield crystalline arsenates. Furthermore, if soluble phosphates produce a precipitate with a given cation, an analogous reaction may be expected with H_3AsO_4 in ammoniacal solution. The usefulness of this reaction is obviously greatly restricted, and it is applicable in the group of the alkaline earths to relatively pure salts of calcium only.

Magnesium gives $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$ identical in habit with the calcium salt. The zinc and cadmium salts are isomorphous with the magnesium salt, and while not so readily obtained in good crystals, may under favorable conditions yield all the crystal forms normally obtained with calcium or magnesium.

Silver yields Ag_3AsO_4 in characteristic deeply colored dendrites, skeletal forms, and tabular crystals, soluble in excess of NH_4OH . (See Silver, page 254.)

The importance of the H_3AsO_4 reaction is chiefly with reference to the ion AsO_4^{---} . When this ion occurs in solutions of complex mixtures, difficultly soluble, more or less crystalline double arsenates are prone to separate in the performance of various "micro" tests for both cations and anions.

H—By Means of Iodic Acid — HIO_3 .¹¹*Compounds Formed* — $\text{Ca}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$ $\text{Sr}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$ $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$.

Iodic acid affords an excellent means of differentiating between salts of calcium, strontium, and barium, providing the salts are fairly pure and the test is made upon dilute solutions containing no free mineral acid.

Apply the reagent by Method I, page 30. According to Denigès, the best results are obtained when the reagent is employed in approximately 10 per cent solution.

With salts of calcium there is slowly formed a very fine precipitate of almost colloidal dimensions; this gradually becomes granular, and appears brown or black in color by transmitted light; if the conditions of concentration are just right tiny pointed "octahedra" are obtained, but more often only disks and flattened spherocrystals, the latter eventually becoming drusy. At room temperature, in neutral solution, the salt $\text{Ca}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$ separates, but from hot solutions or solutions containing free HNO_3 a monohydrated salt is obtained. The hexahydrate has been variously ascribed to both the orthorhombic and the triclinic systems.

Strontium yields a fine granular precipitate, resembling that given by calcium, but this soon changes into masses of slender acicular crystals or slender triclinic (?) prisms of $\text{Sr}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$; the former are grouped in moss-like radiating tufts. The mossy effect is enhanced by many curving bundles of dendritic crystals. By transmitted light these bundles and masses appear brown or black but are snow-white by reflected light. From more concentrated solutions dumb-bell like masses and spherocrystals are obtained (Fig. 53, page 97) and occasionally short rods singly or in X's or even short stout "octahedra" or forms closely resembling those given by calcium. If calcium is also present, the mossy clumps are not obtained.

As in the case of calcium, the monohydrated salt $\text{Sr}(\text{IO}_3) \cdot \text{H}_2\text{O}$ is precipitated in hot solutions and in solutions acidified with HNO_3 .

Barium gives, instantaneously, a heavy white pulverulent precipitate unless the test drop is very dilute with respect to Ba^{++} .

¹¹ Denigès: *Compt. rend.* **170**, 996 (1920); *Bul. Soc. Chim.* (4), **27**, 560 (1920).

In the latter case clumps of characteristic radiating curving acicular crystals of $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ (monoclinic) are obtained (Fig. 52, page 97), quite different in appearance from the mossy masses of the strontium iodate, but if either calcium or strontium is present the test for barium fails.

Magnesium iodate, $\text{MgIO}_3 \cdot 4 \text{H}_2\text{O}$ (monoclinic), is too soluble to separate unless the test drop goes completely to dryness; the same is true of lithium iodate.

Zinc and cadmium each give small brownish disks similar to those formed by calcium and by strontium; these disks develop into spherocrystals, single, in twos, and in botryoidal masses which appear jet black by transmitted light. Rarely, individual and clumps of very fine acicular crystals are obtained.

The majority of the other commonly occurring heavy metals give with iodic acid heavy white curdy or granular precipitates that appear brown or black by transmitted light with low-power objectives; under exceptionally favorable circumstances disks, spherocrystals or botryoidal masses may be obtained.

The only ions which yield well-formed crystalline iodates are Sr^{++} , Ba^{++} , Tl^+ , and Ag^+ , and the radical NH_4^+ . Thallous iodate separates in tiny crosses and dendritic rosettes of characteristic habit, white by reflected light, black by transmitted light. Silver gives fine very slender needles, resembling $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (but not grouped like gypsum) which show a tendency to form star-like radiating masses.

Satisfactory iodate tests, as stated above, can be obtained with pure salts only. With mixtures the amorphous-appearing precipitated iodates either mask the reactions for Sr^{++} , Ba^{++} , Tl^+ , Ag^+ , and NH_4^+ or prevent the separation of recognizable crystals.

Experiments.

(a) — Test with HIO_3 salts of Ca, Sr, and Ba.

I. Other Reactions of the Alkaline Earths.

1—With Fluosilicic Acid.

See Sodium, page 63.

2—With Potassium Antimonyl Tartrate.

See Antimony, page 210.

DETECTION OF MAGNESIUM

The addition of NH_4OH to a HCl solution containing magnesium salts but no NH_4Cl , causes the precipitation of about one half the Mg^{++} as $\text{Mg}(\text{OH})_2$, the other half remaining in solution as the double salt $2\text{NH}_4\text{Cl} \cdot \text{MgCl}_2$; ¹² (Zn^{++} , Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} , behave similarly). In the presence of salts of ammonium no precipitate is usually obtained with NH_4OH .

$(\text{NH}_4)_2\text{CO}_3$ precipitates a basic carbonate in neutral solutions free from ammonium salts, providing the solution is boiled or allowed to stand a long time.

$\text{Ba}(\text{OH})_2$ precipitates $\text{Mg}(\text{OH})_2$ quantitatively only in the absence of salts of ammonium.

Phosphates and arsenates precipitate magnesium quantitatively even in the presence of large amounts of ammonium salts.

A—By Means of Uranyl Acetate — $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$.

Compound Formed — $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$.

This reaction has been discussed at length under Sodium, Method A, pages 52, 57 (Fig. 31, page 53).

Note well that this triple acetate reaction (polysynthetic monoclinic twins) is also given by a number of other cations, whose absence must be proved before a decision can be reached as to the presence of magnesium.

B—By Means of Sodium Phosphate — HNa_2PO_4 — in Ammoniacal Solution.

Compound Formed — $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$.

Certain phases of this reaction and properties of the reaction product have been discussed under Ammonium, page 77.

The detection of magnesium in simple salts is easy, rapid, and certain, since crystals characteristic of magnesium are readily obtained, but the identification of this element in complex mixtures is apt to prove difficult, inasmuch as it is generally associated with other elements which form insoluble phosphates or hydroxides, and which interfere with, or mask, the test for magnesium.

To a large test drop of the moderately concentrated solution to be tested, add a few tiny fragments of NH_4Cl ; stir thoroughly,

¹² Denigès: *Compt. rend.* **175**, 1206 (1922).

then add several fragments of citric acid; warm gently and stir until dissolved. Add a drop of a concentrated solution (or a fragment) of HNa_2PO_4 . Warm gently and stir. Now cause a drop of a strong solution of NH_4OH to flow into the test drop, but do not warm again.

$\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ is first precipitated in a more or less granular condition; this soon changes into dendritic forms and large feathery stars and X's (Fig. 74, page 113), which in turn develop into plates and tabular forms resembling envelopes and finally rectangular orthorhombic prisms, appear. Crystals recalling the roofs of houses are abundant and characteristic (Fig. 75, page 113). This salt is a striking example of the general analytical principle that "digestion" increases the size of a crystalline precipitate and facilitates filtration and washing.

If a precipitate is formed when the HNa_2PO_4 is added, *i.e.*, before making the test drop alkaline with NH_4OH , it is best to decant the supernatant liquid and add the NH_4OH to the decanted drop. The precipitate is set aside for subsequent analysis.

Insufficient NH_4Cl or citric acid may permit the formation of precipitates which may mask the reaction for magnesium. Too much NH_4Cl is objectionable.

The precipitate usually clings tightly to the glass, permitting easy decantation. After decanting dissolve the precipitate in dilute HCl , in which it is very soluble, and reprecipitate with NH_4OH . Characteristic star-like and X-formed feathery crystals are obtained if the original crystals were $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$. These dendritic and skeleton forms are more characteristic of Mg^{++} than the fully developed prismatic crystals.

Double ammonium phosphates of like habit and isomorphous with $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ are formed by Fe^{++} , Mn^{++} , Co^{++} , Ni^{++} , but these salts do not readily separate under the conditions of the test, *i.e.*, when sufficient citric acid is present. If in doubt, decant the supernatant liquor, wash, and test for Fe^{++} by flooding the crystals with a strong solution of $\text{K}_4\text{Fe}(\text{CN})_6$ (see Iron, page 238); for Mn^{++} by covering the crystals with H_2O_2 ; for Co^{++} by treating with $\text{K}_2\text{Hg}(\text{SCN})_4$; for Ni^{++} by covering the crystals with a strong solution of dimethylglyoxime.

Granular or flocculent precipitates may also be obtained from Ca^{++} , Sr^{++} , Ba^{++} , Zn^{++} , Cd^{++} , Sn^{++++} , Pb^{++} , Ag^+ , Cu^+ , UO_2^{++} , Be^{++} , Fe^{+++} , Al^{+++} , Li^+ , rare earths. Part of these ions will

usually be held in solution by the action of the citric acid; part may be precipitated by the HNa_2PO_4 before the NH_4OH is added.

In acid solution there may also appear granular or sandy precipitates of phospho-molybdates, -tungstates, etc., but these should normally dissolve in NH_4OH and not interfere with the subsequent separation of $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.

Li^+ must be absent (see page 88), for if present no satisfactory test for Mg^{++} can be obtained. Under such conditions precipitate the Mg^{++} with $\text{Ba}(\text{OH})_2$,¹³ filter, wash, dissolve the precipitate in very dilute acid, and test the solution for Mg^{++} .

In the analysis of a mixture of absolutely unknown composition, it is usually essential that the search for Mg^{++} be deferred until other tests have been made, *e.g.*, with H_2SO_4 , NH_4OH , $(\text{NH}_4)_2\text{CO}_3$, $\text{H}_2\text{C}_2\text{O}_4$, etc.

It may sometimes happen that $(\text{NH}_4)\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ is precipitated when NH_4OH is added; if so, its characteristic crystal form will be recognized, but it more frequently happens that if both Mg^{++} and PO_4^{---} are present in a complex mixture other cations are also present which form difficultly soluble phosphates, and these phosphates are insoluble in NH_4OH ; under such conditions the detection of Mg^{++} becomes exceptionally difficult. Behrens' suggestion to remove PO_4^{---} by means of SnO_2 formed from metallic tin is not always successful, but should be tried. Acidify with HNO_3 (1 : 2), add a few bits of pure tin foil and heat the preparation; as soon as the reaction has ceased, heat to boiling. Cool and extract the material with dilute HNO_3 , filter and test the filtrate as directed above. The treatment with tin and nitric acid is conveniently performed in the micro-crucible. (See page 15.)

A variant of the phosphate test has been suggested by Martini and Schamis.¹⁴ It consists in substituting cesium for ammonium. To the test drop HNa_2PO_4 and CsCl are added. Tetrahedra of the salt $\text{CsMgPO}_4 \cdot 6 \text{H}_2\text{O}$ are obtained. In our experience this procedure has no advantages over the production of $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.

Experiments.

(a) — Try the phosphate reaction on a solution of MgSO_4 ; then try it on salts of Fe, Mn, Co, Ni, Al, Zn, and Cd. Repeat the experiments, this time adding the HNa_2PO_4 before the NH_4OH .

¹³ Schoorl: *Beiträge*, p. 130.

¹⁴ *Second Chem. Congress Buenos Aires, 1924*, 14.

(b) — Make mixtures, trying various combinations of the above with members of Groups I and II.

(c) — Test for ammonia by means of this reaction as described on page 77.

DETECTION OF ZINC AND CADMIUM

A—By Means of Potassium Mercuric Thiocyanate — $K_2Hg(SCN)_4$.

Compounds Formed — $ZnHg(SCN)_4$

$CdHg(SCN)_4$.

Apply the reagent by Method I, page 30, or by Method II, page 32.

The test appears to be slightly more sensitive when made by Method II, but much better preparations are obtained by Method I.

The reagent drop should be concentrated, but the test drop very dilute and only slightly acid.

Although traces of strong acids do not appear to have a deleterious effect upon the reactions obtainable with $K_2Hg(SCN)_4$, it is always a wise precaution to add a little $NH_4C_2H_3O_2$ or $NaC_2H_3O_2$. A small fragment may be added and the test drop warmed and stirred until the salt has dissolved; a slight excess of alkali acetate is favorable to the production of typical crystals of the double thiocyanates of both zinc and cadmium.

Zinc yields an almost instantaneous precipitation of pure white (colorless) feathery crosses and branching feathery aggregates which appear black by transmitted light (Fig. 76, page 125). From very dilute solutions this salt — $Zn(SCN)_2 \cdot Hg(SCN)_2$ — crystallizes in right-angled orthorhombic prisms or square tablets and fourlings, but under the conditions which usually obtain in testing upon an object slide skeleton and dendritic crystals predominate and prismatic crystals are seldom obtained; the dendrites are, however, peculiar to Zn^{++} , and furnish one of the best, most sensitive, and most reliable micro tests for Zn^{++} at our disposal.

The cadmium salt $Cd(SCN)_2 \cdot Hg(SCN)_2$ separates more slowly in brilliant colorless orthorhombic prisms usually several times as long as broad, one end usually pyramidal, the other beveled or truncated (probably sphenoidal or bisphenoidal); an almost constant peculiarity is the presence of cavities near each end of the prisms (Fig. 77, page 125). As in the case of Zn^{++} , the habit

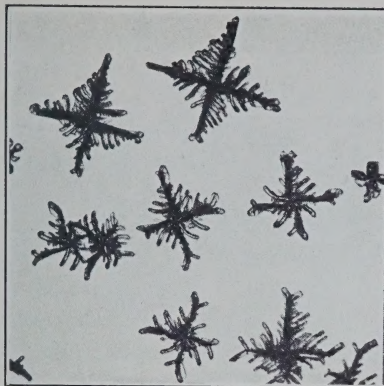


FIG. 76. Zinc with Potassium Mercuric Thiocyanate. 100X.

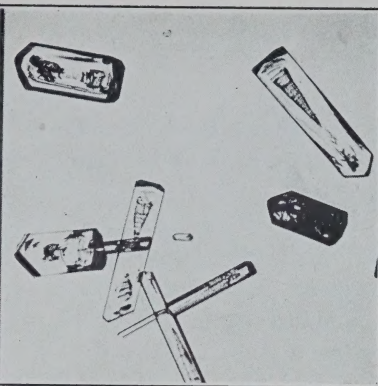


FIG. 77. Cadmium with Potassium Mercuric Thiocyanate. 100X.

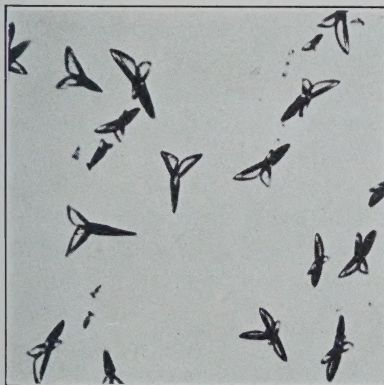


FIG. 78. Zinc + Cadmium with Potassium Mercuric Thiocyanate. 100X.

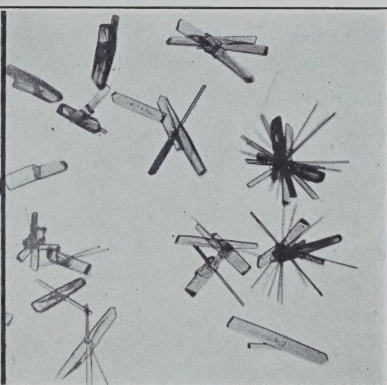


FIG. 79. Cobalt with Potassium Mercuric Thiocyanate. 100X.



FIG. 80. Copper with Potassium Mercuric Thiocyanate. 100X



FIG. 81. Gold with Potassium Mercuric Thiocyanate. 100X.

of the Cd^{++} double thiocyanate is peculiar to the element and thus affords a most valuable test. The prisms are single, and are rarely grouped or in aggregates, unless formed in concentrated solutions.

Copper forms the salt $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2 \cdot \text{H}_2\text{O}$, greenish yellow in color, in mossy dendrites and in fusiform or boat-shaped crystals; radiating groups of pointed prismatic crystals are also abundantly formed (Fig. 80, page 125). The only other element giving a reaction in any way resembling that of copper is gold. The gold salt, whose true composition is unknown, separates in orange or yellow mossy dendrites very similar to the mossy dendrites of copper, but gold forms neither the fusiform, nor the boat-shaped, nor the pointed prismatic crystals that are so characteristic of copper (Fig. 81, page 125); moreover, there appears to be a reduction to metallic gold and the formation of a "gold tree" as the test drop goes to dryness. There is some doubt as to the nature of the reaction, since KSCN produces an identical sequence of crystals in AuCl_3 solutions.

The cobalt salt $\text{Co}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ is quite soluble and therefore separates only as the concentration rises through evaporation. It forms beautiful deep-blue pleochroic ("cobalt blue") star-like groups and radiating masses of imperfectly developed orthorhombic prisms (Fig. 79, page 125).

Nickel gives no reaction unless the test drop is very highly concentrated with respect to Ni^{++} . There will then be obtained tiny yellowish disks and spherocrystals which are almost colorless; the thicker masses of the infinitely fine radiating needles appear brownish by transmitted light (structural color).

Manganous salts under favorable conditions yield colorless irregular slender prisms singly and in masses, somewhat resembling badly formed crystals of the cadmium salt, but readily differentiated because the clear-cut straight-edged prisms terminating in beveled, truncated, or pyramidal faces are not formed (Fig. 83, page 127). From its habit and behavior it is probable that the salt has the formula $\text{Mn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ and is isomorphous with the Zn^{++} , Cd^{++} , and Co^{++} salts. A trace of H_2SO_4 favors the separation of the Mn^{++} salt.

Lead is precipitated as granular crystals without distinguishable form and then only from solutions high in Pb^{++} content; in the latter case it may interfere with the test for Zn^{++} and for Cd^{++}

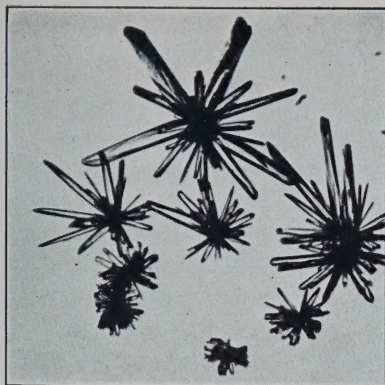


FIG. 82. Lead with Potassium Mercuric Thiocyanate. 100 $\times$.

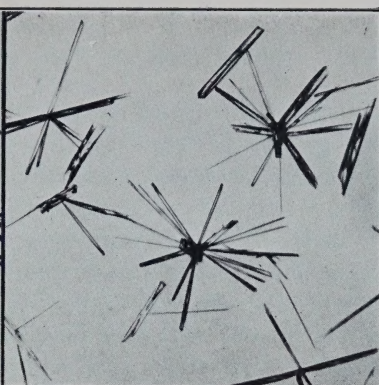


FIG. 83. Manganese (Mn^{++}) with Potassium Mercuric Thiocyanate. 100 $\times$.

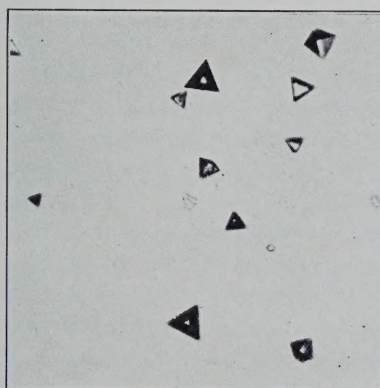


FIG. 84. Zinc with Sodium Bicarbonate. 200 $\times$.

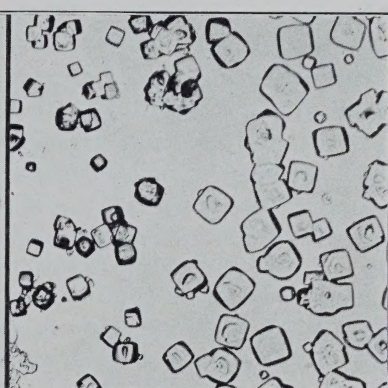


FIG. 85. Zinc with Sodium Nitroprusside. 200 $\times$.

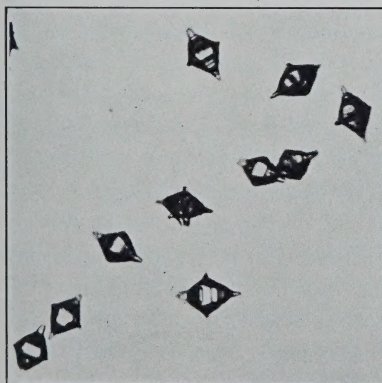


FIG. 86. Cadmium with Cesium Chloride. 200 $\times$.

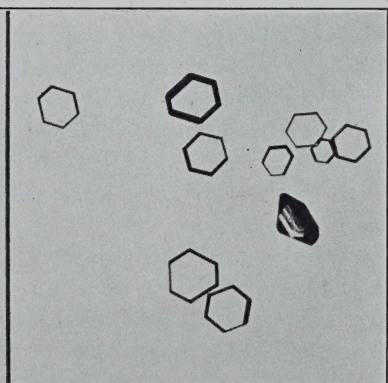


FIG. 87. Cadmium with Cesium Chloride. 100 $\times$.

and therefore should be separated by H_2SO_4 before testing with $\text{K}_2\text{Hg}(\text{SCN})_4$. But if the test drop contains much $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ there may be formed radiating clusters of colorless slender tapering prisms, in outline resembling the blue Co^{++} salt (Fig. 82, page 127).

Silver yields a fine granular precipitate soon developing into tiny, thin, slender prisms with square or oblique ends, at times somewhat resembling the cadmium salt but not to be confused with the latter since the crystals of the silver salt always remain very small. Much silver masks the zinc and the cadmium reactions and must first be removed by precipitation with HCl .

Ferrous salts do not interfere with the test for zinc or for cadmium unless present in an amount equivalent to an almost saturated solution of ferrous salts. There may then separate groups of irregular radiating crystals and masses of feathery or mossy dendrites.

Ferric salts yield at once the blood-red color of $\text{Fe}(\text{SCN})_3$. If more than a mere pink color is produced, the reaction for all the cations above mentioned will be masked either because of the intense color of the solution or because the crystals which separate take up the ferric salt in solid solution and become reddish, reddish-brown or almost black. This is eventually accompanied by a remarkable change into masses of curving, branching, filiform crystals. This latter phenomenon is accentuated if $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$ or $\text{NaC}_2\text{H}_3\text{O}_2$ are present in the drop, which may happen if a marked excess of either of these reagents has been used to mitigate the action of free mineral acids.

No cations other than those above mentioned yield crystals with $\text{K}_2\text{Hg}(\text{SCN})_4$ under the conditions prescribed above, but the descriptions of the solid phases which separate apply only to those cases where the *single* cation is present. In mixtures of these cations a variety of phenomena may be obtained.

It is well to bear in mind that the addition of the reagent to a test drop containing Hg^{++} will be followed by a precipitation of $\text{Hg}(\text{SCN})_2$ which may destroy the reagent or mask a reaction.

In the presence of even a very small amount of cadmium the zinc salt loses its feathery character, though a few large crosses and star-like dendrites may still be formed; more cadmium forces the zinc salt into arrow-head forms (Fig. 78, page 125); still more cadmium gives rise to elongated arrow-heads, slender prisms of irregular outline or thin plates; these pass by very gradual transi-

tions into the typical prisms of the pure cadmium salt. A small amount of zinc in a large amount of cadmium may thus escape detection; but a small amount of cadmium in a large amount of zinc is readily discovered.

Copper usually separates before the zinc salt, but when present in traces only, it colors the crystals of the zinc and the cadmium double thiocyanates without in any way changing their habit. A trace of copper gives a lavender or violet tint; more copper colors the crystals chocolate, brownish, or even black, and drusy spherulites, almost opaque, may appear. In dilute solutions in which the Zn^{++} is in decided excess of Cu^{++} , no crystals of copper mercury thiocyanate are apt to be seen but only crystals of a solid solution of the Cu^{++} salt in the Zn^{++} or Cd^{++} salt. But if the Cu^{++} is in excess of the Zn^{++} , the zinc double salt separates first deeply colored and later the yellow copper salt appears. This is true in dilute solutions only; in more concentrated solutions the copper salt may be the first to appear. The addition of a very little copper acetate to a test drop suspected of containing traces of zinc or cadmium increases the probabilities of detecting these cations.

The cobalt double thiocyanate entering into solid solution in the zinc or cadmium double salts colors them very faintly blue when only a trace of cobalt is present; the intensity of the coloration increases with the rise in Co^{++} concentration until the tint is so dark as to render the crystals almost black. With small amounts of cobalt the feathery zinc mercury thiocyanate crystals are merely tinted blue and the crystal form remains unchanged, but with a rise in the Co^{++} concentration, the zinc salt becomes less and less feathery until the crystals become a solid solution of the zinc salt in the prismatic crystals of cobalt mercury thiocyanate. Owing to the much greater solubility of the cobalt salt than that of the copper salt, the addition of cobalt to a test drop in which zinc or cadmium is sought is of much less value than the addition of Cu^{++} . With much cobalt and little cadmium only the cobalt forms are obtained.

The presence of a high percentage of both Cu^{++} and Co^{++} in solutions containing Zn^{++} or Cd^{++} gives rise to crystals of very peculiar colors and forms which are very different from those obtained when either Co^{++} or Cu^{++} alone is present with the Zn^{++} or Cd^{++} .

The double thiocyanate reaction (first proposed by Behrens) we have found to be the most useful, satisfactory, and generally dependable that has yet been found for the microscopic identification of Zn^{++} , Cd^{++} , Cu^{++} , and Co^{++} . The salt $\text{K}_2\text{Hg}(\text{SCN})_4$ ¹⁵ appears to be a more reliable reagent than a solution prepared by adding NH_4SCN to a solution of HgCl_2 until the precipitate first formed is just redissolved. It is also a more satisfactory reagent than either the ammonium or the sodium double salt.

In a mixture containing two or more elements and in which the percentage of either zinc, cadmium, copper or cobalt is greatly in excess of other elements, the presence of the predominating cation governs the type of crystals formed, and the cations in small amount may be completely overlooked by the analyst unless he is on his guard.

Moreover, in most mixtures containing these elements in almost equal amounts the crystal forms (and colors) are usually completely changed, and are apt to prove at times extremely puzzling. Changes in the appearance of the crystals may be brought about by elements other than those listed above. Such changes, however, serve to indicate at once that more than a simple cation is present in the test drop.

Iodide and other ions yielding precipitates with Hg^{++} interfere with the reactions by destroying the reagent.

When much nickel and very little cobalt is present the reaction for cobalt is apt to fail.

For complicated cases such as those just referred to there can be no "guide" outlined, but for simple mixtures the following tabulation may prove useful.

The material is dissolved in concentrated HNO_3 and evaporated to dryness to remove any tin and to remove iodide and other anions which might destroy the reagent. The residue is treated with HNO_3 and again evaporated. If a white residue (metastannic acid) is obtained, extract with dilute HNO_3 , decanting or filtering. Evaporate the solution carefully to dryness at a low temperature, add water — if a precipitate or turbidity results (Bi, Sb), decant or filter. If lead or silver are probably present add HCl to the filtrate and filter. To the filtrate add $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_2$ and $\text{K}_2\text{Hg}(\text{SCN})_4$ as directed on page 124.

¹⁵ Chipman, Ruth E., Unpublished Thesis, Cornell University, 1917. See Appendix, page 394.

There results:

A—A white dense precipitate without any definite crystal form:

Au or Cd in too concentrated solution.

Pb, Ag, Mn, Ni, Hg.

Treat as in *B*.

B—Make a very dilute solution and test again:

a—Feathery pure white (black by transmitted light) crosses, X's and irregular feathery dendrites: Zn.

b—Colorless, clean-cut, straight-edged prisms, with pyramidal or beveled ends: Cd.

c—White, granular precipitate or tiny skeleton crystals and plates: Pb. Confirm by HCl or KI.

d—White and colorless arrow heads and irregular crystallites: Zn, and any or all of the following: Cd, Ni, Mn.

C—The Zn crystallites are blue: Zn and Co.

The Cd prisms are blue: Cd and Co.

Blue crystallites and arrow-heads: Zn, Cd, and Co.

Dark-blue, tapering, radiating prisms: Co, and any or all of the following: Zn, Cd, Ni, Mn.

D—The Zn crystallites are lavender, brown or black: Zn and Cu.

The Cd prisms are lavender or brown: Cd and Cu.

Irregular crystallites, brownish blue or bluish green: Zn (and possibly Cd, Ni, Mn) with Cu and Co.

E—Lemon-yellow, mossy dendrites and elliptical plates or fusiform crystals: Cu.

F—Golden, mossy dendrites with a metallic luster; no fusiform prisms or plates: Au.

G—The solution is colored pink or red: Fe. (Or red or brown crystals in a red solution.)

Experiments.

(a) — Apply the thiocyanate reagent, in the manner indicated, to solutions of pure Zn salts of different degrees of concentration.

(b) — Try in turn pure salts of Cd, Cu, Co, Ni, Ag, and Pb.

(c) — To a Zn solution add a very little Cd and test. Repeat the experiment, using more Cd.

(d) — In like manner try mixtures of Zn and Cu; Zn and Co; Zn and Fe; Zn and Mg; Zn and Al; Zn and Pb; Zn and Ag.

(e) — Then try more complex mixtures, as, for example: Zn, Cd, and Cu; Zn, Cd, and Co; Au, Cu, and Co; etc.

In each case prepare several slides under different conditions and note well the changes in the appearance in the crystals which separate.

B—By Means of Sodium Bicarbonate — HNaCO_3 .*Compound Formed* — $3 \text{Na}_2\text{CO}_3 \cdot 8 \text{ZnCO}_3 \cdot 8 \text{H}_2\text{O}$.

This sodium-zinc salt can be obtained by several different procedures: addition of a saturated solution of HNaCO_3 to a neutral test drop, or to a drop made ammoniacal with NH_4OH , or to a drop made strongly alkaline with NaOH . All three methods give excellent results with pure salts of zinc, but none are wholly dependable when dealing with mixtures such as alloys containing zinc. In the presence of cadmium the procedure using NaOH is alone reliable.

The salt $3 \text{Na}_2\text{CO}_3 \cdot 8 \text{ZnCO}_3 \cdot 8 \text{H}_2\text{O}$ separates slowly in the form of small colorless triangular plates and isotropic tetrahedra (Fig. 84, page 127). Three-armed and five-armed dendrites are also formed, the arms of which generally terminate in tetrahedra. Short stout prisms with pointed ends are also formed. The tetrahedra are constant and peculiar to zinc; no other element yields similar crystals with HNaCO_3 .

There is first precipitated by the reagent a fine formless precipitate consisting of a basic carbonate of zinc; this salt in the presence of an *excess* of alkali carbonate is slowly transformed into the characteristic sodium zinc carbonate. This latter salt adheres firmly to the object slide, permitting easy decantation and washing. It can then be dissolved and subjected to other confirmatory tests.

Since a large number of cations are precipitable by alkali carbonates, forming bulky compounds, the reaction for zinc is often completely masked, or if not, the habit of the sodium zinc carbonate may be so modified that the test becomes unreliable. To avoid these difficulties Schoorl¹⁶ has suggested the following procedure. To the dilute solution to be tested, sufficient NaOH is added to convert the precipitated zinc hydroxide into sodium zincate which passes into solution. To insure solution add a slight excess of NaOH and stir thoroughly. Decant, centrifuge, or filter (through asbestos). Then add to the filtrate HNaCO_3 in a *very fine* powder, in slight excess, so that some of the solid alkali carbonate remains undissolved in suspension. Thorough stirring is essential, but care must be used to avoid rubbing the glass slide during the stirring or there will result an immediate precipitation of submicroscopic crystals upon the surface of the glass. These tiny crystals rarely develop into recognizable forms.

¹⁶ *Beiträge z. mikrochem. Anal.* p. 105.

After the stirring the preparation should be set aside for a few minutes in order to allow time for the growth of typical crystals.

If the solution is too dilute no crystals will appear until sufficient evaporation has taken place to permit the separation of the double salt. Concentration of the test drop by heating after the addition of the reagent is not permissible.

If Schoorl's method is followed cadmium does not interfere with the test for zinc since a soluble carbonate is not readily formed.

In mixtures of cadmium and zinc, if no separation of the zinc is attempted but the reagent HNaCO_3 added at once, a cadmium double carbonate is precipitated, with or before the zinc, in granular form masking the zinc reaction.

Behrens¹⁷ has shown that it is possible to differentiate between zinc and cadmium by adding an excess of HNaCO_3 to an ammoniacal test drop. The cadmium double carbonate separates first, and if the supernatant liquor is decanted before the zinc salt separates, typical tetrahedra can be found in the decanted solution after it has stood for a short time. Satisfactory results are obtainable with comparatively simple mixtures only, since the alkaline earths, members of Group VIII, etc., are also precipitated with the zinc and cadmium.

Experiments.

(a) — Try precipitating Zn in neutral and in ammoniacal solutions. Try decantation from the precipitate.

(b) — Test mixtures of Zn and Cd, first in neutral and then in ammoniacal solutions.

(c) — Experiment with Zn in the presence of the interfering elements noted above.

C—By Means of Oxalic Acid — $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$.

Compounds Formed — $\text{ZnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$

$\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$

The reagent is applied by Method I to the neutral or slightly acid test drop, which should be moderately concentrated.

$\text{ZnC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ separates as small double spherulites or as tiny pseudo-octahedra singly or united end to end in twos; thin rhombs are also formed (Fig. 64, page 109). It is rare that a preparation

¹⁷ Behrens: *Anleitung*, 2 Auf. p. 52. Behrens-Kley: *Mikrochem. Anal.* p. 70. This method requires skill and experience, and reliable results are possible under the most favorable conditions only.

can be obtained in which well-formed, clear-cut crystals can be found. The usual habit is that of grains with rounded angles or disks, appearing as if the crystals had begun to dissolve.

Under a low power the crystals of zinc oxalate often bear a striking resemblance to the imperfectly developed oxalates of calcium and strontium. It is therefore unwise to place dependence upon an oxalate precipitate alone, if zinc is being sought.

Cadmium, on the other hand, gives clear, colorless, well-developed monoclinic prisms and tabular crystals of the salt $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ (Fig. 65, page 109). The prisms are usually thin, long, and narrow, with square or more often obliquely truncated ends, the acute angle being about 60° . The extinction angle (with long edge) is 24° (Haushofer). The prisms occur singly in X's and in irregular radiates consisting of lath-shaped crystals of greatly varying sizes. The tabular crystals are, in outline, rectangular or unsymmetrical, elongated hexagons. From very concentrated solutions octahedral crystals are obtained in addition to the prisms and plates.

The typical prismatic crystals of $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ are obtainable only when dealing with almost pure salts of cadmium. Very small percentages of zinc do not seriously interfere, but when the ratio of zinc to cadmium exceeds 1 : 10 the prisms are shortened and as the proportion of zinc increases the precipitate takes on the habit of zinc oxalate and no indication of the presence of cadmium is obtained.

Manganese gives $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$, which separates in radiates closely resembling those of the cadmium salt, but more regular and star-like (Fig. 69, page 109). Some of the prisms have pointed, some square, and some obliquely truncated ends. The acute angle of truncation although less than that in the cadmium salt is too close to it to be useful as a means of differentiation. $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ can be distinguished from $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$ since it is very strongly birefringent, exhibits brilliant polarization colors and extinguishes *parallel* to the elongation of the prisms.

Mixtures of zinc and cadmium, zinc and manganese, cadmium and manganese, give mixed crystals whose appearance varies with the relative proportion of these elements. In most cases the appearance is such that the experienced analyst can form a fairly reliable opinion as to the nature of the mixture with which he is dealing.

Free mineral acids are objectionable.

The test may be masked by the presence of salts of silver, lead, mercury, tin, copper, and trivalent metals.

More than traces of magnesium usually seriously modify the habit of the oxalates of both zinc and cadmium.

For data relative to oxalates which may separate when oxalic acid or alkali oxalates are used as reagents, see page 105.

Alkali oxalates may be substituted for oxalic acid, thus slightly increasing the delicacy of the test but not improving the character of the crystals which separate.

D—By Means of Sodium Nitroprusside¹⁸— $\text{Na}_2\text{NOFe}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$.

Compound Formed — $\text{Zn} \cdot \text{NOFe}(\text{CN})_5 \cdot \text{H}_2\text{O}(?)$

The best results are obtained when the reagent is applied by Method I to a neutral test drop of moderate concentration. A small amount of free mineral acid is in no way objectionable, but much acid causes a complete change in the habit of the crystals.

Zinc forms a nitroprusside of low solubility and is precipitated at once in spherical grains, botryoidal masses, and in tiny circular disks having a faintly brownish color but usually so thin as to appear to be colorless. On long standing the spherical grains develop a large number of faces, and grains can be found which show what appear to be faces of the cube, octahedron and dodecahedron and combinations of these (Fig. 85, page 127). The crystals are isotropic. The formula of the compound has not been definitely established.

In distinctly acid solutions there may be formed rectangular prisms, square plates, and fusiform rods.

Heat hastens the reaction but does not produce better-formed crystals.

Cadmium yields tiny drusy globulites, octahedra with rough, corrugated, or bristling faces, and drusy aggregates. The crystals are strongly birefringent, and the larger ones exhibit brilliant polarization colors. Their behavior toward polarized light provides a means of easily differentiating between cadmium and zinc.

Mixtures of cadmium and zinc yield rough globulites not to

¹⁸ Bradley: *Am. J. Sci.* **22**, 326 (1906). This test was developed for the identification of zinc in shellfish, and according to its originator is the only specific micro-test for zinc in material of this sort.

be distinguished from the first-formed drusy globulites of cadmium. Such mixed crystals are generally anisotropic.

Mn^{++} forms a nitroprusside that cannot be distinguished from that of Zn^{++} ; both have the same habit, are of like size, and both are isotropic.

With Cu^{++} there is first formed an "amorphous" pale-blue precipitate in which later there may develop star-like skeleton crystals. Mixtures of Cu^{++} and Zn^{++} yield the "amorphous" blue precipitate and the spherical grains and disks of Zn^{++} , but the zinc salt in this case resembles the cadmium salt more closely than the typical forms of zinc, but are readily differentiated since they are isotropic.

Ni^{++} forms a flocculent light-green precipitate and Co^{++} a similar pink one. Iron (unless very concentrated) gives no reaction unless the preparation is heated and then a yellow deposit only.

Mercurous salts are precipitated as a yellowish, gelatinous mass.

Hg^{++} , Ag^{+} , Pb^{++} , Sn^{++} , Sn^{++++} , Sb^{+++} , Bi^{+++} , Al^{+++} , Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} give no precipitates and yield no crystalline salts even in high concentrations or on evaporation almost to dryness.

When using sodium nitroprusside as a reagent, if no reaction is obtained on the first test, repeat using a much more concentrated test drop. Then heat the preparation. A precipitate indicates the presence of Zn^{++} , Cd^{++} , Ni^{++} , Fe^{+++} , Mn^{++} , or Cu^{++} . If no precipitate is obtained these elements are absent.

E-By Means of Rubidium Chloride or Cesium Chloride.¹⁹

Compounds Formed — $4 \text{RbCl} \cdot \text{CdCl}_2$

$4 \text{CsCl} \cdot \text{CdCl}_2$.

A-When RbCl is employed as reagent it should be added by Method III, page 34. This method or that of covering the dry residue with a drop of the reagent (Schoorl) is essential if characteristic crystals are to be obtained. Of the two methods the authors prefer the first or "streak" method. The reagent drop should be almost saturated.

$4 \text{RbCl} \cdot \text{CdCl}_2$ crystallizes in a variety of forms in which color-

¹⁹ Rimbach: *Ber.* **35**, 1306 (1902).

Schoorl: *Beiträge z. mikrochem. Anal.* p. 70.

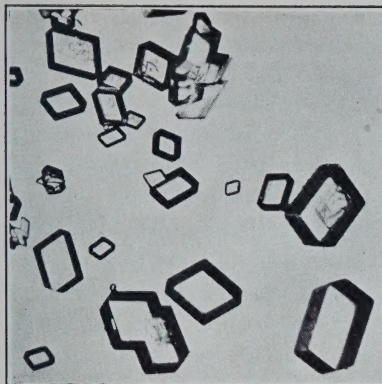


FIG. 88. Cadmium with Rubidium Chloride. 150 $\times$.

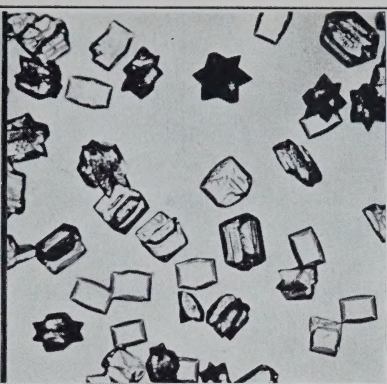


FIG. 89. Cadmium with Rubidium Chloride. 200 $\times$.

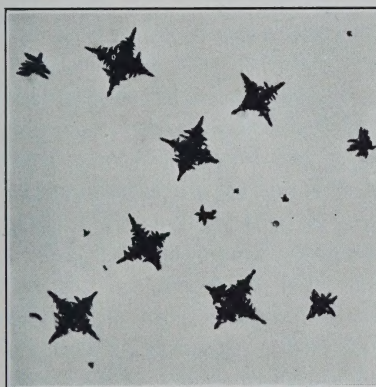


FIG. 90. Mercury (Hg^+) with Potassium Bichromate. 100 $\times$.

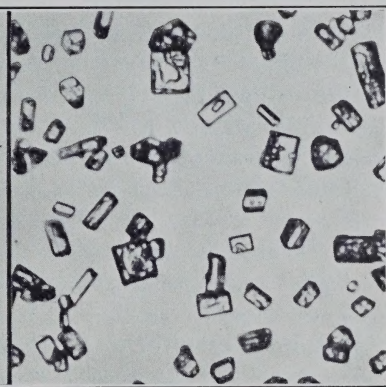


FIG. 91. Mercury (Hg^{++}) with Potassium Iodide. 300 $\times$.

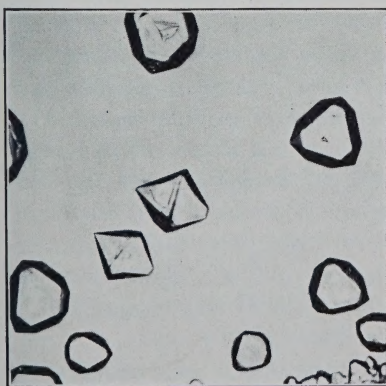


FIG. 92. Aluminum with Cesium Sulphate. 100 $\times$.



FIG. 93. Aluminum with Ammonium Fluoride. 200 $\times$.

less, highly refractive, well-developed rhombohedral tablets predominate (Fig. 88, page 137). Short, stout, hexagonal prisms with pyramidal or blunt ends are also formed. These prisms are weakly birefringent with parallel extinction. Curious barrel-shaped aggregates, strongly birefringent, are almost always present (Fig. 89, page 137). The rhombohedral tablets have their angles so near 90° and so many of them lie in a position in which they are isotropic that they are not readily distinguished from plates of RbCl. In many preparations six-sided plates and tablets separate in large numbers. In such crystals two of the opposite and parallel sides are much shorter than the other four. Symmetrical hexagons are rare (distinction from Sb^{+++} and Bi^{+++}). These six-sided tablets, if carefully focused, cannot be confused with such cubes of RbCl as lie in a position yielding a six-sided image in the microscope.

Since we are dealing with a dry residue prismatic crystals are almost always present. To avoid confusion the search for characteristic crystals of the double salts should be confined to a zone well inside the reagent channel. $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ forms monoclinic lath-shaped crystals and long thin prisms with square ends, singly, in aggregates, or in sheaf-like bundles. They are strongly birefringent and most of them show parallel extinction.

Characteristic crystals of $4 \text{RbCl} \cdot \text{CdCl}_2$ are seldom obtainable from cadmium salts other than the chloride. Although the nitrate can be made to yield a satisfactory test, it is always wise to evaporate repeatedly with concentrated HCl if the material to be analyzed contains nitrates or has been brought into solution with HNO_3 or with aqua regia. If cadmium is present as a sulphate the test is unreliable or fails.

The rubidium zinc chloride is so very soluble that it does not separate until the channel of the reagent passes to dryness, and even then well-formed crystals are not likely to be obtained.

The usefulness of the rubidium chloride test for cadmium is very limited because RbCl forms double chlorides with the chlorides of a large number of elements, many of which are to be found associated with cadmium. Some of these double chlorides are of about the same solubilities as the rubidium cadmium salt. Moreover, RbCl is a reagent rarely used and the analyst is seldom familiar with its many double salts.

B—Considered from all points of view, CsCl appears to be a

more useful reagent than RbCl for the identification of cadmium, but its successful use is more closely dependent upon carefully controlled conditions than is the case with RbCl .

The reagent is best applied by Method I, page 30. The test drop should be moderately concentrated (see page 82) and free from an excess of acid. The cadmium must be present as chloride, not as sulphate. The reagent drop must be an almost saturated solution of CsCl .

The compound formed is probably $4 \text{CsCl} \cdot \text{CdCl}_2$. It separates first in tiny highly refractive grains or tiny crystals which appear to be octahedra but which will be found on careful focusing to be hexagonal bipyramidal twins (distinction from Cs_2SnCl_6) (Fig. 86, page 127). These twins consist of hexagonal pyramids united at their basal planes; many of them soon elongate into what appear to be stout bipyramidal prisms with a prominent swelling midway in their lengths and with many marked cross striations; they are very characteristic and are specific for cadmium. Single pyramids with their basal planes in contact with the glass slide develop into isotropic hexagonal plates and tablets (Fig. 87, page 127).

No separation of crystals is obtained with zinc until the preparation has stood for some time and evaporation has carried the test drop nearly to dryness (*i.e.*, to complete saturation with respect to the cesium zinc chloride). Under these conditions, if much zinc is present, large, colorless, imperfectly developed prisms and tablets of the cesium zinc salt may appear. These crystals have parallel extinction, are strongly birefringent, and show brilliant polarization colors. The reaction is of no value for the identification of zinc, for the crystals of the double salt are not characteristic and their solubility is too high.

Mixtures of cadmium and zinc give the typical bipyramidal twins of cesium cadmium chloride unless the zinc is greatly in excess of the cadmium.

Since cesium chloride forms double chlorides of low solubilities with many elements, there are many possibilities of interferences; the analyst must therefore be on his guard lest he misinterpret a reaction.

CsCl applied to the test drop by Method III as is practiced with RbCl is prone to yield unsatisfactory results because of the immediate formation of a granular precipitate or of hexagonal plates

and tablets to the exclusion of the more typical bipyramidal twins.

The following tabulation of the more readily formed double chlorides of cesium may aid the analyst in differentiating between cations which may be encountered in mixtures.

Colorless Apparently Isotropic Cesium Double Chlorides.

<i>Octahedra</i>	Cs_2SnCl_6	Cubic
	$\text{CsCl}\cdot\text{HgCl}_2$	Cubic (mostly cubes)
<i>Hexagonal Plates and Tablets</i>	$\text{CsCl}\cdot\text{CdCl}_2$	Hex.
	3 $\text{CsCl}\cdot 2 \text{TiCl}_3$	Hex.
	2 $\text{CsCl}\cdot\text{SbCl}_3\cdot 2\frac{1}{2} \text{H}_2\text{O}$	Hex.
	3 $\text{CsCl}\cdot 2 \text{BiCl}_3\cdot 2\frac{1}{2} \text{H}_2\text{O}$	Hex.
	3 $\text{CsCl}\cdot 2 \text{SbCl}_3$	Hex.

Colored Apparently Isotropic Cesium "Double Chlorides" (These salts are in reality Cs^+ salts of complex Chloro-acids).

<i>Octahedra</i>	Yellow Cs_2TeCl_6	Cubic
	Yellow or brown Cs_2PdCl_6	Cubic
	Yellowish-green Cs_2OsCl_6	Cubic
	Orange Cs_2PtCl_6	Cubic
	Red Cs_2IrCl_6	Cubic
	Brown Cs_2RuCl_6	Cubic
<i>Hexagonal Plates and Tablets.</i>	Yellow 2 $\text{CsCl}\cdot\text{FeCl}_3\cdot\text{H}_2\text{O}$	Hex.

Colorless Anisotropic Cesium Double Chlorides.

" <i>Octahedra</i> "	3 $\text{CsCl}\cdot\text{InCl}_3\cdot 2 \text{H}_2\text{O}$	Tetrag.
<i>Rhombic Plates and Tablets</i>	3 $\text{CsCl}\cdot\text{BiCl}_3$	Ortho.
	2 $\text{CsCl}\cdot\text{InCl}_3$	Ortho.
<i>Rhombohedral Plates and Tablets</i>	4 $\text{CsCl}\cdot\text{PbCl}_2$	Hex.
	$\text{CsCl}\cdot\text{CdCl}_2$	Hex.
<i>Needles, Prisms, Plates, or Tablets</i>	2 $\text{CsCl}\cdot\text{AgCl}$	Ortho.
	$\text{CsCl}\cdot\text{MgCl}_2\cdot 6 \text{H}_2\text{O}$	Ortho.
	$\text{CsCl}\cdot\text{CdCl}_2$	Hex.
	3 $\text{CsCl}\cdot\text{ZnCl}_2$	Tetrag.
	2 $\text{CsCl}\cdot\text{ZnCl}_2$	Mono.
	2 $\text{CsCl}\cdot\text{HgCl}_2$	Ortho.
	4 $\text{CsCl}\cdot\text{PbCl}_2$	Ortho.
	2 $\text{CsCl}\cdot\text{SbCl}_3\cdot 2\frac{1}{2} \text{H}_2\text{O}$	Hex.
	3 $\text{CsCl}\cdot 2 \text{SbCl}_3$	Hex.
	3 $\text{CsCl}\cdot\text{BiCl}_3$	Ortho.
	2 $\text{CsCl}\cdot\text{SnCl}_4$	Ortho.
	$\text{CsCl}\cdot\text{CeCl}_3$	

*Colored Anisotropic Cesium Double Chlorides.**Needles, Prisms, Plates or**Tablets*

Yellow	2 CsCl·CuCl ₂ ·2 H ₂ O	
Orange		
or	CsCl·CuCl ₂	
Red		
Blue	3 CsCl·CoCl ₂	Tetrag.
Green	3 CsCl·NiCl ₂	Tetrag(?)
Red	2 CsCl·FeCl ₃ ·H ₂ O	Hex.
Pink	2 CsCl·MnCl ₂ ·H ₂ O	Triclin.
Yellow	2 CsCl·UO ₂ Cl ₂	Triclin.
Yellow	2 CsCl·RuCl ₃	
Yellow	CsCl·AuCl ₃ · $\frac{1}{2}$ H ₂ O	Ortho.

A number of the formulas given above are in doubt. In the case of most of the chlorides combining with CsCl to form crystallizable double chlorides several double chlorides are possible, depending upon the relative concentrations of the two chlorides. Usually only one of these double salts appears in a given test upon a microscope slide. The authors have chosen the formulas which appear to be closest in accord with the descriptions and analyses which have been published.²⁰

DETECTION OF MERCURY

Preliminary Tests. — Since mercury forms two series of salts, mercurous and mercuric, the problem before the analyst is not only the detection of mercury, but he must also decide whether monovalent or divalent mercury is present or a mixture of the two. Mixtures are frequent because of the instability of most mercury salts. A further complication enters into the already difficult problem because mercury is very prone to form "basic" salts of variable composition.

Test a minute fragment of the unknown material for solubility. (See page 4.) If insoluble, touch a fragment with a tiny drop of dilute KOH; mercurous compounds turn black because of formation of Hg₂O; mercuric salts turn orange yellow (HgO). If, on the other hand, the substance is water-soluble, test as indicated in Method C.

²⁰ For comprehensive discussions of the double chlorides of cesium likely to be met with in microscopic qualitative analysis, the reader is referred to:

Vermande: *Pharm. Weekblad* **55**, 1131 (1918).

Ducloux: *Mikrochemie* **2**, 108 (1924).

A-General Methods Based Upon the Reduction to Metallic Mercury and Subsequent Identification.— Acidify the solution with HCl; introduce into it a tiny piece of pure copper foil or wire 0.5 mm. in diameter and 2 to 3 mm. long. The copper must be bright and clean.²¹ Or a similar tiny piece of magnesium may be employed.

The solution is then gently heated for a few minutes over the micro-burner or on a water bath or hot plate. The small crucible described on page 15 will be found convenient.

The metallic mercury set free by the action of the copper or magnesium amalgamates with the metal. The copper becomes silvery white and the magnesium silvery or black if sufficient mercury is present to "plate" the metal.

In any event the metal fragment is carefully removed, thoroughly washed and dried, and dropped into a capillary tube closed at one end, made by drawing out a clean piece of glass tubing of high melting point. (See Fig. 27, page 44.) Heat the amalgamated metal in the micro-flame until the glass becomes red hot. The mercury will sublime upon the walls of the tube in the form of a grayish ring. Cut the tube at *C* and examine the sublimed mercury under the microscope. Using a bit of glass rod drawn down to the dimension of a hair, rub the film so as to cause the droplets to flow together, examine again and note that larger globules of mercury have been formed. Study the preparation by both transmitted and reflected light so as to be assured that the droplets are opaque, spherical, and exhibit the silvery white luster of metallic mercury. If in doubt, heat the ring of sublimate and thus resublime the mercury.

Confirm the test by converting the mercury into HgI_2 . This may be readily accomplished by holding the tube horizontal and pushing a tiny fragment of iodine into the capillary tube so that the iodine lies about 5 mm. distant from the globules of mercury. Heat the iodine very carefully so as just barely to vaporize it. Set the tube aside for a short time and heat it again at the point where the iodine lies. Yellow metastable and red stable HgI_2 are formed, the former usually rapidly changing into the latter. The change from the red to the yellow pseudo-tetragonal, rhombic

²¹ Rubbing with fine emery paper or similar abrasive or dipping in dilute HNO_3 and washing with distilled water will yield a satisfactory surface.

form, takes place at about 126° .²² The transformation is enantiotropic, and can be readily followed under the microscope. Scratching the yellow dendritic masses when their temperatures have fallen below the transition point causes their immediate transformation into the bright-red stable HgI_2 . When the heating and cooling have not been too rapid, rectangular plates and prisms, bipyramidal prisms and irregular dendritic masses are obtained. HgI_2 melts at 223° to a yellowish-red and finally a red liquid, but the compound sublimes in part before the point of complete fusion is reached. On cooling there is obtained a yellow mass that changes to red. A compound of copper and mercury, $\text{HgI}_2 \cdot \text{CuI}$, behaves in a similar manner, but the change from red to yellow takes place below 100° .

A sublimate of metallic mercury can also be obtained when a dry mercurial salt is heated with anhydrous Na_2CO_3 or with anhydrous CaO . The dry powdered salt of mercury is thoroughly mixed with twice its weight of *freshly ignited* Na_2CO_3 or CaO ; the mixture is introduced into a tube of the type shown in Fig. 27 and compacted by tapping the tube gently; a little of the reagent is then placed on top of the mixture, the tube above freed from material clinging to the sides, and the mixture heated, the temperature is *slowly* raised until the mixture becomes red hot and the tube begins to melt. Mercury will be set free and will sublime. Study the sublimate and test as above.

The examination of a sublimate is facilitated if the tube is laid upon an object slide and a large drop of oil of cedar wood (immersion oil) is flowed over the tube at the point where the sublimate has condensed. The annoying refraction image of the glass tube is thus eliminated.

Experiments.

(a) — Test several mercurous and mercuric salts by heating them with Na_2CO_3 . Examine the sublimes. Rub them gently with a hair-like glass rod and note that the globules unite.

(b) — Obtain a deposit of Hg upon a tiny bit of Cu foil — 1 mm. by 3 mm. — by heating in a drop of a solution of an Hg salt acidified with HCl. Dry and sublime.

(c) — Introduce a fragment of iodine in one or more of the tubes, warm gently and allow to stand about five minutes. Examine for crystals of HgI_2 .

²² Groth: *Elemente d. physikalischen u. Chemischen Krystallographie* (Munich, 1921), p. 318.

B-Test the Solution with Hydrochloric Acid — HCl. — To the very dilute solution add the reagent (1 : 4) by Method I.

Mercurous compounds yield at once a very insoluble, dense, white, somewhat granular precipitate in which no definite crystal form can be discerned even with a high power unless the test drop is exceedingly dilute; then under favorable conditions there may be obtained very tiny slender needles.

Decant and wash the precipitate with warm water. Cause a drop of strong NH_4OH to flow over the white precipitate of HgCl ; it turns black owing to the formation of a mixture of Hg and HgClNH_2 .

This compound, when examined with a high power,²³ will be seen to consist of a mass of tiny acicular crystals, tiny square and rectangular plates, and many fusiform grains.

If the quantity of precipitate is sufficient, decant again and wash, then treat the black compound with a saturated solution of $(\text{NH}_4)_2\text{SO}_4$, in which HgClNH_2 is soluble but metallic mercury is insoluble; the latter can be made to unite into characteristic globules.

Mercuric salts give no precipitate with HCl.

Silver is thrown down as a dense, curdy, white precipitate of AgCl which rapidly darkens under the influence of light. AgCl is readily soluble in NH_4OH from which it separates, on standing, in isotropic rectangular plates, cubes and octahedra (Fig. 171, page 327). Similar cubic crystals can be obtained, but less readily, by boiling the curdy AgCl with concentrated HCl; treated in this way HgCl is also dissolved but separates on cooling in tetragonal plates and prisms, *but no cubes*, and part of the HgCl is oxidized to HgCl_2 .

Lead forms difficultly soluble PbCl_2 separating in colorless, or white, long acicular irregularly ragged prisms, feathery dendritic masses, and X's with characteristic slightly curving arms (Fig. 104, page 169). PbCl_2 is more soluble in water acidulated with HNO_3 than in pure water, hence its separation is far from complete; it is readily soluble in hot water from which, on cooling, it

²³ Cover the preparation with a cover-glass. Great care must be exercised to prevent the objective from coming into contact with the strongly ammoniacal solution, since both copper and nickel are soluble in this reagent. Even NH_3 vapors will attack the objective mount. After using NH_4OH it is wise to wipe off the objective with lens paper moistened with water and then wipe thoroughly dry.

separates in thin, well-formed orthorhombic prisms, pseudo-hexagonal tabular rhombs, and rhombic or six-sided plates (Fig. 105, page 169). Precipitated cold or recrystallized from hot water, the character of the crystal forms obtained will vary with concentration, temperature, and the nature of other metallic ions that may be present. If recrystallized by heating in the presence of salts of the alkalis, double salts are formed which separate on cooling with a very different habit from that of PbCl_2 ; it is therefore better to decant the mother liquor from the PbCl_2 which has been precipitated cold, and recrystallize the crystalline residue, rather than heat the test drop as it stands. If in doubt as to the nature of the recrystallized salt, add a fragment of KI; characteristic iridescent yellow plates of PbI_2 will be formed if lead is present (Fig. 106, page 181).

With thallium (Tl^+), TlCl is obtained, separating in white irregular crosses, or clusters of radiating crystals somewhat star-like in appearance (Fig. 101, page 169); cubes and hexagons are also obtained. Since these crystals are generally aggregates that scatter light they appear black by transmitted light. TlCl is soluble in hot water from which it separates on cooling in transparent (or black in appearance) isotropic cubes. KI precipitates TlI in forms isomorphous with TlCl . The precipitate in the cold is generally sufficiently characteristic for the differentiation of Tl^+ from Pb^{++} , but recrystallization from hot water (after decantation) plus the addition of KI should remove all cause for doubt.

A source of possible error in concentrated solutions may be caused by the separation of complex chlorides of antimony and bismuth; but if the material has been dissolved in HNO_3 , concentrated to crystallization, and a drop of water added, the immediate precipitation of antimonyl or bismuthyl salts should be sufficient warning to the analyst to be on his guard.

Tungstates and molybdates in certain concentrations are decomposed by HCl (and other mineral acids), tungstic acid and molybdic acid being precipitated. (See page 219.)

In all testing with HCl as precipitating reagent the dilute acid should be used, for an excess of concentrated HCl, especially if added to concentrated solutions of salts, will cause the separation of many of them because of the forcing back of their dissociation.

Experiments.

- (a) — Precipitate HgCl ; examine with the microscope.
- (b) — Add NH_4OH to the white precipitate and examine again.
- (c) — Precipitate AgCl , and PbCl_2 , and compare their appearances with that of HgCl .

C-Test the Solution with Potassium Iodide — KI . — (Or with NaI .)*Compounds Formed* — HgI
 HgI_2 .

To the moderately concentrated solution add the reagent by Method I, page 30, but in this case the concentration of the reagent should be low, at least at the beginning of the reaction.

Mercurous salts yield a greenish formless mass of HgI which is soluble in an excess of KI with the formation of $2 \text{KI} \cdot \text{HgI}_2$ and some metallic mercury is usually set free.

Mercuric salts yield brilliant vermilion-red HgI_2 in tiny rhombs, cubes, rods, rectangular plates, and tablets, rosette-like dendritic aggregates, or botryoidal masses. These crystals belong to the tetragonal system (Fig. 91, page 137).

When the flow of the reagent into the test drop is sufficiently slow yellow metastable HgI_2 is first formed which changes almost at once into the stable red iodide. If the concentration of the reagent is too high HgI_2 is immediately dissolved and a colorless solution of $2 \text{KI} \cdot \text{HgI}_2$ results. HgI_2 is also soluble in an excess of mercuric salts, hence a low concentration of reagent and a high concentration of Hg^{++} in the test drop may prevent a satisfactory crystallization of HgI_2 . It may thus happen that unless the preparation is closely watched and carefully performed, no evidence of the presence of Hg^{++} may be obtained even if much mercury is present; moreover, many other alkali salts and most ammonium salts dissolve HgI_2 because of its property of uniting with them to form double salts.

To guard against the possibility of error it is usually wise to add to the preparation (after the KI has flowed in) a tiny fragment of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. The copper will unite with the I^- of the KI , thus breaking down the double mercury salt and causing the precipitation of red HgI_2 in its characteristic form.

Lead forms PbI_2 , bright yellow flakes and characteristic hex-

agonal plates (Fig. 106, page 181). These plates when floating and at the proper angle appear greenish or brownish by transmitted light, sometimes even gray. By reflected light they exhibit the brilliant colors of thin films, an extremely characteristic feature of this compound.

Silver is precipitated as AgI in a faintly yellow formless mass; but if the KI has been added in excess a crystalline compound may separate.

Thallium (Tl^+) usually gives merely a fine granular precipitate appearing black by transmitted light, but if conditions are just right crystals similar in appearance to those of $TlCl$ are obtained. (See Fig. 101, page 169.)

Cuprous salts give cuprous iodide, a dense white granular precipitate. Cupric salts under certain conditions may also give cuprous iodide and set free iodine, the latter appearing as opaque black more or less granular and rhomb-shaped crystals. In dark-green solutions the white iodide may appear to be greenish, resembling HgI .

Salts of antimony in the presence of HNO_3 may yield with KI orange-red crystals, some of which closely resemble those of HgI_2 , but most of the crystals are hexagonal plates or six-pointed rosettes — the skeletons of the hexagonal plates. This iodide is soluble in KI solutions, giving a double iodide whose solubility is sufficiently low to cause it to separate in the test drop in the form of large yellow plates and prisms, singly or more often in bristling aggregates and sheaves or star-like masses. In testing with KI solutions containing antimony, iodine is generally set free and a test for mercury may be unobtainable.

Bismuth salts in solution react somewhat like antimony, but since the tendency to form basic salts (bismuthyl salts) is greater than in the case of antimony, more acid (usually HNO_3 or HCl) is required to keep a clear solution and consequently iodine is more readily set free and in greater quantity; it follows that bismuth iodide and crystalline double iodides are less readily obtained. Most compounds of arsenic behave like bismuth.

Cadmium, antimony, bismuth, arsenic, and lead interfere with or mask the iodide test for mercury.

Certain compounds of selenium and tellurium give an orange-red or brownish-red crystalline precipitate with KI. (See page 148.)

The behavior of potassium iodide with some of the commoner elements can be summarized as follows:

<i>Character of precipitate:</i>	<i>Elements which may be present:</i>
Brilliant red crystals	Hg. (Red HgI_2 becomes yellow on heating.)
Orange-red crystals	(Hg); Cd; Sb; Bi; As; Se; Te; Sn^{++++} .
Yellow iridescent plates	Pb.
Yellow needles, plates and prisms	Pb; Sb; (Bi?).
Greenish granular mass	Hg; Cu^+ ; Cu^{++} .
White or very faintly yellow curdy mass or granular precipitate	Ag; Cu^+ ; Cu^{++} ; Cd(?); Tl $^+$.
Brownish-red pulverulent precipitate or tiny dark red (almost black) disks, with iodine set free	Hg; Sb; Bi; As; Se; Te; Tl $^+$.
Opaque black plates, needles, and dendritic fragments. Solution yellow	Iodine, set free from KI; Pd.

In testing percussion powders for mercury (fulminate) and antimony (sulphide) it should be borne in mind that powerful oxidizing agents (KClO_3) may interfere with the ordinary tests. The powder should be "spread out" and the various components picked out under a hand lens or Greenough-type binocular microscope.

Experiments.

(a) — Precipitate HgI_2 with KI. Note the effect of adding an excess of the reagent. Then add CuSO_4 to remove the excess iodide.

(b) — Add KI to a solution of HgNO_3 .

D-To the Solution add Potassium Thiocyanate and Zinc Sulphate.

Compound Formed — $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$.

Mercurous salts give no characteristic reaction; but mercuric salts yield $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ (Fig. 76, page 125). This compound has already been discussed under zinc. (See page 124.)

The addition of a little copper or cobalt acetate greatly increases the sensitivity of the reaction.

To perform the test, proceed as follows. To the moderately concentrated neutral test drop add a small fragment of KSCN ; stir thoroughly. If a precipitate is formed, add more reagent. Place adjacent to this drop, a drop of water in which is dissolved

a very little $\text{ZnSO}_4 \cdot 5 \text{H}_2\text{O}$ and a *trace* of a copper or cobalt salt. Cause the test drop to flow into the zinc solution. If mercury is present, characteristic crystals of $\text{Zn}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ will appear. These crystals will be colored by the copper or the cobalt as has already been described. (See Zinc, page 124.)

When dealing with relatively pure salts of mercury this test leaves little to be desired, but in complex mixtures, it is difficult properly to adjust the concentration of the KSCN ; this is especially true if a precipitate is obtained which does not dissolve in an excess of the reagent. When the test drop is turbid, it is best to decant, centrifuge, or filter before the drop is caused to flow into the drop containing the zinc or cobalt.

Experiments.

See under Zinc, Method A, page 131.

E-Test the Solution with Potassium Bichromate — $\text{K}_2\text{Cr}_2\text{O}_7$.

This reaction should be regarded as a confirmatory test for the presence of mercurous compounds rather than one useful for the identification of mercury. Its sensitivity is very low and there are many interfering elements and conditions. The reaction, however, is a most interesting one, particularly from the viewpoint of crystallization phenomena.

The test drop should be concentrated with respect to Hg^+ and should be strongly acidified with HNO_3 (1 : 4). The reagent may be added by Method I or by Method II to the test drop at room temperature, or heated to the boiling point; in the latter case there is danger of oxidizing Hg^+ to Hg^{++} .

Mercuric compounds yield no crystalline precipitate.

Mercurous salts are precipitated as mercurous chromate Hg_2CrO_4 . There is first formed a dark-red (black by transmitted light), fine, granular precipitate which immediately develops into spherical grains, disks, and globular masses, these in turn become drusy and grow into irregular aggregates of radiating short stout prisms with rounded or angular ends or crosses and dendrites are formed (Fig. 90, page 137). In a few minutes aggregates closely resembling lichens are formed. These lichen-like aggregates and the skeletal crosses are very characteristic.

If the reaction has been performed by Method II in a hot solution, thin square plates and crosses predominate. These plates

show the colors of thin films and appear lemon yellow by transmitted light. If the preparation contains an excess of the mercurous salt and is boiled there may be formed a basic salt²⁴ $\text{Hg}_2\text{O} \cdot 2 \text{Hg}_2\text{CrO}_4$ crystallizing in dark-red needles.

Lead precipitated in hot HNO_3 solutions gives crystalline aggregates closely resembling those of Hg_2CrO_4 , but most of the crystals are rhombs and tiny well-formed prisms. These crystals are soluble in NaOH (distinction from Hg_2CrO_4).

Silver yields large dark-red pleochroic plates and scales which may often mask the test for Hg^+ . (See Silver, page 252; Fig. 170, page 327.)

Strontium, barium, cadmium, zinc, and manganese yield insoluble or difficultly soluble chromates and therefore interfere.

Experiments.

Test with $\text{K}_2\text{Cr}_2\text{O}_7$ as above both mercurous and mercuric salts, with and without HNO_3 present, in both cold and hot solutions.

DETECTION OF BERYLLIUM

A—By Means of Chloroplatinic Acid — H_2PtCl_6 .

Compound Formed — $\text{BePtCl}_6 \cdot 8 \text{H}_2\text{O}$.

The test is performed by Method III, page 34. In order that the results may be satisfactory, it is essential that the dry film shall contain a high concentration of beryllium and that members of the group of the alkalis shall be absent or present in little more than traces.

$\text{BePtCl}_6 \cdot 8 \text{H}_2\text{O}$ separates in hygroscopic, faintly yellow, square and rectangular plates and rectangular prisms of the tetragonal system (Fig. 51, page 81). The crystals usually occur singly, but penetration twins are also formed; their solubility is somewhat less than that of $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and their separation from solution can be induced by the addition of alcohol. This is most easily accomplished by applying a large drop of alcohol to the object slide near the test drop and immediately tipping the slide so as to cause the drop of alcohol to flood the preparation. Holding the slide well inclined prevents the alcohol from spreading over the whole surface, and in a few seconds it may be placed on the microscope stage for examination.

²⁴ Fichter and Oesterheld: *Zeit. anorg. Chem.* **76**, 347 (1912).

If the addition of the reagent causes an immediate precipitation of the potassium group, an excess of the reagent should be added, the solution decanted from the precipitated chloroplatinates, and more chloroplatinic acid added to the decanted liquid in order to assure a sufficient excess. Evaporation must be resorted to and even then $\text{BePtCl}_6 \cdot 8 \text{H}_2\text{O}$ will seldom crystallize well unless the air of the laboratory is very dry. Usually it is necessary to use alcohol in which the beryllium salt is much less soluble.

The crystalline residue obtained should always be examined with crossed nicols. Beryllium chloroplatinate exhibits parallel extinction and is only weakly birefringent; the corresponding sodium salt is strongly birefringent, shows brilliant polarization colors and oblique extinction (triclinic). The potassium group give isotropic salts. (See Potassium, page 66.)

In our experience this test for beryllium is valueless unless the material tested is so high in beryllium as to constitute a fairly pure salt of this element.

B-By Means of Potassium Oxalate — $\text{K}_2\text{C}_2\text{O}_4$.

Compound Formed — $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{BeC}_2\text{O}_4$.

To the moderately concentrated neutral test drop add a little acetic acid; then add the potassium oxalate by Method II, page 32, but in this case the fragment of reagent must be more than twice as large as is usual in microscopic analysis.

$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{BeC}_2\text{O}_4$ separates in large, stout, clear, colorless, monoclinic prisms; singly, in twins, or in groups of radiating, irregularly formed prisms. Thin plates in the form of rhombs are also obtained. The salt is strongly birefringent and exhibits an extinction angle of about 39° (Fig. 63, page 103).

Unless the reagent is present in sufficient excess the test is apt to prove unsatisfactory. Acid potassium oxalate or the oxalates of sodium or ammonium are not suitable reagents.

During the disintegration and solution of the reagent fragment well-formed crystals of $\text{K}_2\text{C}_2\text{O}_4$ usually appear *momentarily*. These crystals often bear a striking resemblance to the double salt, and it is therefore imperative that the analyst shall be on his guard lest he fall into error through too hasty a decision.

Certain salts (*e.g.*, HgCl_2), if present in the drop being tested, have the property of inducing potassium beryllium oxalate to

crystallize in long prisms. Behrens²⁵ has therefore suggested that a little HgCl_2 be added to the test drop before the fragment of reagent is introduced in order to assure the formation of elongated prisms, thus differentiating the double salt from crystals of $\text{K}_2\text{C}_2\text{O}_4$.

Many other elements form normal or double oxalates. (See Calcium, page 105.)

$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{BeC}_2\text{O}_4$ can be readily recrystallized by gently warming the preparation until the salt passes into solution, on cooling, large well-formed characteristic crystals are obtained. These crystals are soluble in a solution of ammonium carbonate, a property which can be made use of when there is doubt as to the nature of the compound obtained.

TREATMENT OF MIXTURES — SECONDARY GROUP OF GROUP II

(a)—*Test for PO_4^{---}* by molybdate method, page 197. If phosphates are present, remove the PO_4^{---} by treatment with tin in HNO_3 solution, proceeding as follows. Add strong HNO_3 , then a few pieces of *pure tin* foil or granulated tin. Boil until all the metallic tin has been converted into insoluble metastannic acid. Decant, or filter, and repeat the treatment until no test for PO_4^{---} is obtained. Evaporate the solution to dryness and test a portion for arsenic. If arsenic is found, ignite the residue until all arsenic is driven off. Extract the residue with water acidified with HNO_3 and test as below.

In order that the removal of all the PO_4^{---} may be successfully accomplished, it is essential that the concentration of the HNO_3 in the test drop shall be sufficiently high and that no excess of metallic tin shall have remained undissolved.

The treatment is best performed in the small glass crucible shown in Fig. 6, page 15, or in a tiny test-tube rather than attempted upon an object slide or in a small watch-glass.

(b)—*Remove the alkaline earths, lead, and silver*, by precipitation with H_2SO_4 ; filter; evaporate the filtrate and fume off the excess of H_2SO_4 .

(c)—*Separation of Beryllium*. — Treat the weakly acidified drop with iron foil to remove metals more electro-negative than iron. (See page 373.)

Add NH_4OH and H_2O_2 ; warm gently for a time, evaporate and

²⁵ *Anleitung*, p. 45. Behrens-Kley: *op. cit.*, p. 48.

repeat the treatment. Extract the residue with a concentrated solution of $(\text{NH}_4)_2\text{CO}_3$. Be^{++} , Zn^{++} , U^{++++} , Mg^{++} may be present in the solution. Evaporate, dissolve in dilute HCl , add a little acetic acid, and test with $\text{K}_2\text{C}_2\text{O}_4$.

If much Mg^{++} is present, add to the acid solution NaOH , in which Mg^{++} is insoluble; the solution may contain Be^{++} , Zn^{++} , Al^{+++} .

(d)—*Separation of Magnesium from Beryllium, Zinc, Cadmium and Aluminum.* — Precipitate with NaOH , warm, evaporate, extract the residue repeatedly with small amounts of water. Mg^{++} and some Cd^{++} remain undissolved. Dissolve the insoluble portion in HCl and divide into two portions; test one portion for Mg^{++} with HNa_2PO_4 and the other for Cd^{++} by the thiocyanate method.

(e) *Separation of Zinc from Beryllium, Magnesium and Cadmium.* — Ignite the material *gently*, and warm with a strong solution of NaOH . Zn^{++} and Be^{++} are dissolved. Decant, acidify with acetic acid and precipitate the Be^{++} as oxalate. (Some Zn^{++} is always precipitated with the Be^{++} .) Decant, evaporate the clear solution to dryness and destroy the oxalate ion by H_2SO_4 and heat. Take up the residue with water (acidify if necessary), add $(\text{NH}_4)\text{-C}_2\text{H}_3\text{O}_2$ and test for Zn^{++} by the thiocyanate method, (page 124).

(f)—*Separation of Beryllium from the "Rare Earths."* — To a moderately dilute solution add oxalic acid and boil. Be^{++} remains in solution, the rare earths and Zn^{++} are precipitated; or advantage can be taken of the fact that BeSO_4 is soluble in excess of K_2SO_4 .

(g)—*Separation of Beryllium from Aluminum.* — Add $(\text{NH}_4)_2\text{CO}_3$ in excess. Both Al^{+++} and Be^{++} are at first precipitated, but the $\text{Be}(\text{OH})_2$ is soluble in excess of $(\text{NH}_4)_2\text{CO}_3$. Repeat the precipitation and re-resolution several times.

CHAPTER V

THE DETECTION OF THE ELEMENTS OF GROUP III

B; Sc, Y, La, Yt; Al, Ga, In, Tl

Group III of the Periodic Classification of the elements comprises (1) the transitional element boron, (2) a group of the rare earths, scandium, yttrium, lanthanum, and ytterbium, (3) the aluminum group comprising aluminum, gallium, indium, and thallium.

Boron is essentially an acid-forming element, and it is rare indeed that the analyst is called upon to detect boron in material other than borates. The borates which the analyst is apt to encounter in his work are salts of HBO_2 —metaboric acid, H_3BO_3 —orthoboric acid, $\text{H}_2\text{B}_4\text{O}_7$ —tetraboric acid (also sometimes called diboric acid) and HBO_3 —perboric acid.

The element boron resembles carbon and silicon, but in its salts the resemblance approaches beryllium, aluminum and scandium; in spite of these resemblances, however, we have no boron compounds related to these elements suitable for microchemical identity reactions.

The only compounds of sufficiently characteristic habit are derivatives of the acid HBF_4 ; but unfortunately, the alkali salts of the acid are isomorphous with the corresponding fluosilicates, fluotitanates, fluozirconates, and fluogermanates, and hence can be of but limited value in the analysis of complex mixtures.

The elements falling in the sub-group consisting of scandium and the "rare earths" have practically no analytical analogies with the reactions employed for the identification of members of the other sub-group of Group III, but react more like the alkaline earths. Since it is not practicable to discuss the chemical properties of the scandium group without considering also that group of the rare earths not readily classified in the Mendeléef Periodic Table, we have thought it wise to defer all consideration of the rare earths until after the elements of Group VIII have been discussed. On pages 280–285 will be found a presentation of the properties

upon which the microscopical detection of the rare earths can be based.

The elements in the aluminum group, consisting of aluminum, gallium, and indium, are all closely related; they (especially indium and gallium) also behave in some respects like beryllium, zinc, and cadmium, but their identification tests bear little resemblance to the elements of Group II. In their stable salts they are trivalent, and because Group III approaches the center of the Periodic Table acidic properties begin to make their appearance. Most of their salts hydrolyze if boiled in neutral aqueous solution. The hydroxides of aluminum, gallium, and indium are readily soluble in strong solutions of NaOH and KOH,¹ forming compounds of the type $M(\text{ONa})_3$ or $M(\text{OK})_3$. These compounds exhibit a marked difference in stability. The aluminates and gallates are quite stable, but $\text{In}(\text{OH})_3$, though apparently passing into solution in NaOH or KOH, separates on standing and is immediately precipitated on warming. Gallium hydroxide differs from $\text{Al}(\text{OH})_3$ and $\text{In}(\text{OH})_3$ in being readily soluble in NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ and is even soluble (but with difficulty) in Na_2CO_3 and K_2CO_3 solutions.

When the members of the aluminum group occur singly their property of forming easily crystallizable double sulphates — “alums” — affords one of the most satisfactory reactions for their recognition. But obtaining the characteristic crystals of an alum is merely indicative of the presence of one or more of a group of elements. The general formula of these isotropic double sulphates is $N_2\text{RO}_4 \cdot M_2(\text{RO}_4)_3 \cdot 24 \text{H}_2\text{O}$ — or simplified, $NM(\text{RO}_4)_2 \cdot 12 \text{H}_2\text{O}$, in which N may be Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , Tl^+ , or NH_4^+ ; M , Al^{+++} , Ga^{+++} , In^{+++} , Tl^{+++} , Cr^{+++} , Mn^{+++} , Fe^{+++} ; and R , S , or Se . All these double sulphates are isotropic and form an isomorphous series.

The members of the aluminum group form with the salts of the alkalis a large number of double salts other than the “alums.” With the exception of the “alums” these double salts are nearly all anisotropic; many of them crystallize readily and have a sufficiently characteristic habit to render them of analytical value.

With HF and the alkali metals double fluorides are formed, some of which can be utilized to good advantage, especially in the

¹ Providing chromium is absent; see Chromium, page 214.

analysis of silicates and siliceous materials where simpler and more convenient methods are not practicable.

The element thallium, like the other elements of high atomic weight, gold in Group I, mercury in Group II, and lead in Group IV, differs markedly in chemical properties from the characteristic properties of the group in which it falls. Thallium forms two series of salts, thallos (Tl⁺) and thallic (Tl⁺⁺⁺); the latter are unstable in aqueous solution and change into thallos compounds if their solutions are boiled. In analytical practice we are concerned with solutions containing thallos compounds only.

Thallium resembles the elements of the potassium group in the formation of an isotropic difficultly soluble chloroplatinate, Tl₂PtCl₆; it resembles Ag⁺, Hg⁺, and Pb⁺⁺ in forming a chloride, bromide, and iodide of low solubility; it resembles the alkaline earths, silver (and lead) in that it forms a sulphate of somewhat low solubility. Its analogy to aluminum is shown by its property of forming "alums." Thallium is the strongest base in Group III, the basicity in the vertical groups increasing with the atomic weight.

DETECTION OF BORON

A—By Means of Turmeric (Curcumin).

Compound Formed — "Rosocyanine."

The reagent is applied by Method VI, page 37.²

Place a drop of the solution to be tested upon an object slide. Acidulate with dilute HCl, to decompose any borates present and set free boric acid. Introduce into the drop thus prepared a piece of the reagent-carrying fiber about 5 mm. long, being sure to immerse it completely in the liquid. Allow the drop to evaporate spontaneously to complete dryness, or hasten the evaporation by *very gentle* warming. Cool and examine the fiber under the microscope. A rose or violet-rose color is indicative of the presence of boron. To confirm the reaction place upon the dry fiber a drop of a one per cent solution of NaOH; the rose color should immediately change to a clear Prussian blue which in turn gradually becomes violet and pleochroic.³ There appear to be no interferences other than those given below.

² The preparation of viscose rayon fibers impregnated with curcumin is described on p. 396.

³ Chamot and Cole: *Ind. Eng. Chem.* **10**, 48 (1918).

Too high a temperature during evaporation or failure to allow the test drop to go completely to dryness may lead to negative results.

Too high a concentration of the alkali will interfere with the formation of the blue color, and since the clear blue color is quite fugitive if only traces of boron are present, it is essential that the fiber be examined *immediately* after the application of the NaOH.

Mineral acids, other than boric acid, give a yellow or brown color to the fiber on evaporation; furthermore the addition of the alkali produces a deep brown, never a blue color.

Hygroscopic salts should be absent since they prevent complete drying of the fiber, but if much boron is present the test may succeed in the presence of considerable retained moisture.

Powerful oxidizing (bleaching) substances must be absent, or their characteristic properties must be destroyed before adding the reagent fiber.

Much free phosphoric or silicic acid interferes with the test, rendering the detection of boron exceptionally difficult.

Since this test for boron is extraordinarily delicate ($0.025 \mu \text{ g.}$) object slides containing no boron must be used. It is also obvious that glassware containing boron must never be used in preparing or handling material that is subsequently to be tested for the presence of boron. It is therefore wise always to perform a "blank" test in order to be assured of the purity of the reagents and apparatus employed.

Free boric acid can be differentiated from borates by evaporation in contact with the fiber without the addition of the HCl, but the absence of all acids or salts capable of setting free boron must have been ascertained. It must also be borne in mind that certain organic acids have the power of replacing boric acid in borates.

Ferric salts, particularly if present as ferric borate, interfere with the curcumin reaction.

The rose-colored compound, which turns blue with alkalis, was given the name "rosocyanine" by Schlumberger;⁴ its true structure is still in doubt, but it is known that it contains no boron.

⁴ *Bull. soc. chim.* (2) **5**, 194 (1866).

B—By Means of Ammonium Fluoride and Potassium or Cesium Chloride.

Compounds Formed — KBF_4
 CsBF_4 .

To the concentrated solution, add a large fragment of NH_4F ; stir with a platinum wire until the NH_4F is dissolved; next add a drop of HCl (1 : 2), and finally add a crystal fragment of KCl or CsCl . The entire operation must be performed upon a celluloid slide. After standing several minutes orthorhombic crystals of the double salt begin to separate in the form of square, rectangular, and rhombic plates, which grow into tabular crystals with beveled edges; these in turn elongate and become rectangular prisms with square or pyramidal ends. (See Fig. 94, page 159. The preparation from which this photograph was made was allowed to pass to dryness.) Their refractive index is so close to that of the mother liquor (between 1.32 and 1.34) that they are almost invisible and require very careful adjustment of the illumination to disclose their true form. The sodium salt, like that formed with silicon, sometimes exhibits the Christiansen effect. (See Sodium, page 63.)

In order that the crystals may be more readily found it is best to allow the preparation to stand and evaporate to dryness and thus eliminate the effect of the refractive index of the mother liquor.

Instead of double salts we may properly consider that we have to deal with salts of fluoboric acid HBF_4 . The ammonium, potassium, rubidium, and cesium salts appear to be isomorphous.

The cesium fluoborate test would be an excellent one were it not that a number of other elements form, with cesium salts and HF , compounds of sufficiently low solubility to separate on the object slide. Hence the usefulness of the test is restricted to confirmation only, and is of little value in complex mixtures containing any of the interfering elements discussed below.

Aluminum is precipitated as Cs_3AlF_6 in tiny cubes too small to be resolved with safety,⁵ but if KCl is substituted for CsCl well-

⁵ Very minute crystals are objectionable as a test where HF is present, since they require a high-power objective for their recognition and the free working distance of such objectives brings the front lens so close to the drop as to endanger the front lens of the objective. The preparation should always be covered with thin celluloid or viscose.

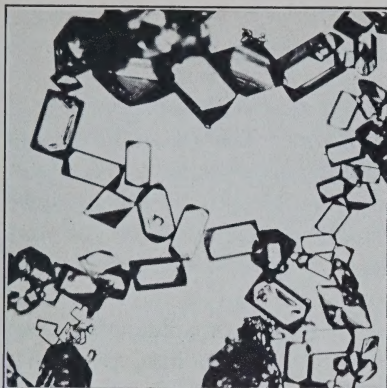


FIG. 94. Boron with Potassium Fluoride. 200 $\times$.

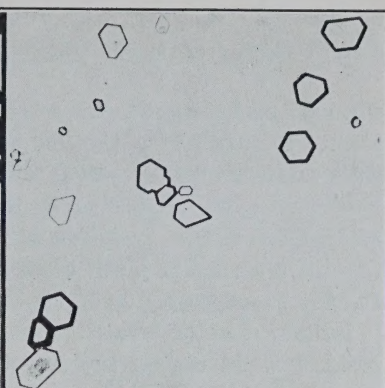


FIG. 95. Germanium with Potassium Fluoride. 200 $\times$.

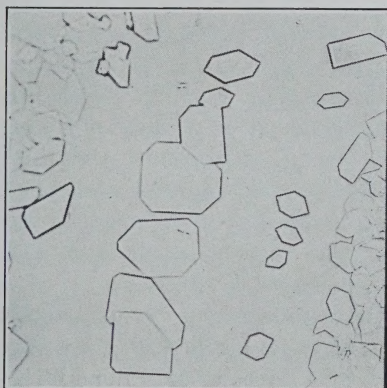


FIG. 96. Titanium with Potassium Fluoride. 100 $\times$.

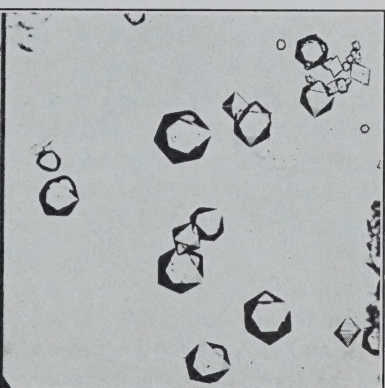


FIG. 97. Zirconium with Ammonium Fluoride and Rubidium Chloride. 100 $\times$.

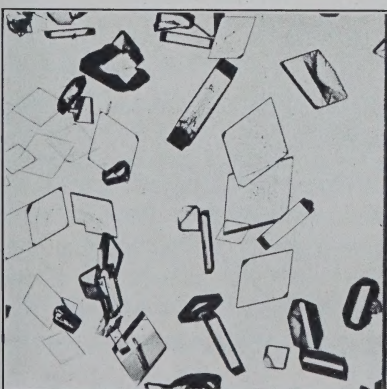


FIG. 98. Indium with Cesium Chloride. 100 $\times$.

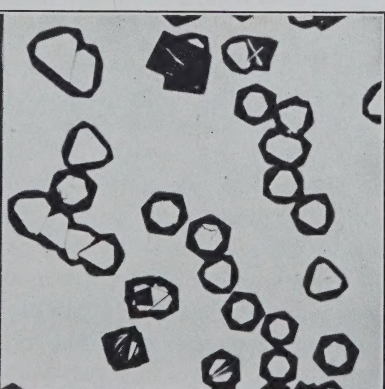


FIG. 99. Indium with Hexamethylenetetramine. 150 $\times$.

formed octahedra and cubes are formed, of sufficient size to constitute a satisfactory test for aluminum. The potassium group salts are isomorphous; their solubilities decrease with the rise in atomic weight; all belong to the cubic system, but the sodium salt is monoclinic. K_3AlF_6 is probably a double salt $3 KF \cdot AlF_3$ but may be regarded as a salt of the hypothetical fluoaluminic acid — H_3AlF_6 .

Indium chloride treated as above rarely gives a fluoindate, but yields instead cesium indium chloride. (See Indium, page 165; Fig. 98, page 159.)

Gallium gives a granular precipitate of a fineness so great, even in dilute solutions, as to appear to be non-crystalline; occasionally a preparation may be obtained in which there can be seen tiny irregular sandy grains more or less rounded, single, or so grouped as to resemble tiny rods.

Titanium, chromium, iron, and vanadium also form with the potassium group and HF, compounds analogous to those of boron and aluminum; but zirconium, silicon, germanium, and lead form salts derived from the hypothetical acid H_2RF_6 . Considering the compounds as double salts, their composition may be expressed by the formula $2 MF \cdot RF_3$ where M is an alkali metal and R either Zr, Si, Ge, or Pb. (See Figs. 95, 96, 97, page 159.)

In testing materials of unknown composition, with an alkali salt and HF, we may expect, as the drop goes to dryness, that any of the above double salts may make their appearance. In addition to this troublesome feature there is another, already referred to; namely, that in this group of fluorine compounds, the refractive indices are all so nearly those of the mother liquors as to render difficult the recognition of the salts.

DETECTION OF THE ELEMENTS OF THE ALUMINUM GROUP, Al, Ga, In

These three elements are so closely related in their chemical behavior that their microchemical identification is very difficult in material in which two or more are present, especially when one of them is in minute amount only. This is particularly true if the quantity of material available for analysis is also small; for although separation methods on a test-tube scale are practicable,

these same methods applied to drops of solution are rarely dependable.

The usual procedure is based upon differences in the solubilities of the hydroxides, but these hydrous oxides are so easily peptized or changed into negative sols that extraordinary difficulty may be met in dealing with these compounds in drops on an object slide. Moreover, the presence of organic acids will usually prevent the precipitation of the hydroxides.

The group is precipitated with NH_4OH in the presence of NH_4Cl , only sufficient NH_4OH being used to keep copper, nickel and cobalt in solution, if these elements are present. Gallium may be lost in this treatment. The precipitated hydroxides must be washed with water containing a little NH_4Cl to avoid peptization.

Theoretically the separation should then not be difficult, for warming the hydroxides with NaOH or KOH should yield soluble aluminates, gallates, and indates, and the indate first formed should hydrolyze on heating and be reprecipitated as $\text{In}(\text{OH})_3$. The difficulty arises in the practical impossibility of properly adjusting concentrations when dealing with mere traces of precipitates. The second step is based upon the fact that $\text{Ga}(\text{OH})_3$ is readily soluble in $(\text{NH}_4)_2\text{CO}_3$ solution, but $\text{Al}(\text{OH})_3$ is insoluble in this reagent. Since zincates and cadmates may be formed in the treatment with fixed alkalis, it is always essential to test for the presence of these elements before attempting a separation of the aluminum group.

This hydroxide separation, though practicable, is never sharp and leaves much to be desired.

Gallium can be separated from aluminum and indium by precipitation with $\text{K}_4\text{Fe}(\text{CN})_6$ in a HCl solution. Filter or centrifuge and wash the precipitate with warm HCl . Dissolve the precipitate in aqua regia; evaporate to small bulk; add HCl and heat until all oxides of nitrogen are expelled. Neutralize with $\text{NaC}_2\text{H}_3\text{O}_2$, add acetic acid and precipitate iron by a solution of alphanitrosobetanaphthol in 50 per cent acetic acid. Filter or centrifuge. Make the filtrate alkaline with NH_4OH and boil until $\text{Ga}(\text{OH})_3$ is precipitated.⁶ Wash, dissolve in H_2SO_4 and test with Cs_2SO_4 and with $\text{K}_4\text{Fe}(\text{CN})_6$.

⁶ Papish and Holt: *Jour. Phys. Chem.* **32**, 145 (1928).

A—By Means of Cesium Sulphate — Cs_2SO_4 .*Compounds Formed* — $\text{Cs}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ $\text{Cs}_2\text{SO}_4 \cdot \text{Ga}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ $\text{Cs}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}.$

To the drop to be tested NH_4OH is added to precipitate the hydroxide, the supernatant liquid is decanted and the precipitate washed once.⁷

To the precipitate dilute H_2SO_4 is added a *very little* at a time until the precipitate is practically completely dissolved, but using care to avoid an excess of acid. If too concentrated a solution is obtained, add a drop of water.

To the test drop thus obtained, add the Cs_2SO_4 by Method II, page 32.

Cesium “alum” separates in large, well-formed, brilliant, colorless octahedra, or combinations of the cube and octahedron (Fig. 92, page 137). Elongated octahedra and octahedra flattened parallel to two diagonally opposite faces are also common.

In solutions that are too concentrated or that have evaporated too rapidly, dendritic forms and many-faced crystal aggregates are obtained. In such cases decant the mother liquor, and recrystallize the residue from warm water.

Solutions of the “alums” have a tendency to supersaturate, and such metastable solutions may pass to complete dryness without showing individual crystals. Recrystallization must then be resorted to; sometimes several trials are necessary before characteristic octahedra are obtained.

A metastable state can usually be avoided by spreading out the test drop into a large thin drop before the cesium salt is added and then crushing the reagent in the drop immediately it is added. As soon as alum crystals begin to form, crush one or more with a glass rod and draw the crushed material across the drop.⁸

Isotropic double sulphates crystallizing in octahedra are formed by elements other than aluminum, gallium, and indium, as has

⁷ This method of procedure, *i. e.*, precipitation of the hydroxide and subsequent solution in the proper acid, should always be followed in all tests for Al^{+++} , Ga^{+++} , and In^{+++} .

⁸ Schoorl has suggested inoculating the test drop with a very minute fragment of cesium alum, thus “seeding” the preparation and inducing crystallization. It has also been suggested to perform the test on an object slide where a little cesium alum has previously been crystallized and carefully washed off with hot water.

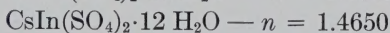
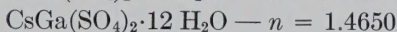
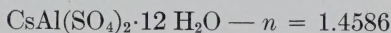
been discussed on page 155. The preliminary precipitation with NH_4OH and solution of the precipitate will generally yield evidence as to the presence of these other alum-forming elements — Cr, Fe, Tl, Mn.

Although this test affords no differentiation between aluminum, gallium, and indium, the last two elements are so rare in ordinary practice that the cesium alum reaction may be considered as the most satisfactory identity test for aluminum now available. If there are reasons for suspecting that gallium or indium may be present, separate the hydroxide as outlined on page 161.

The cesium indium alum is much more soluble than the isomorphous cesium aluminum compound and is therefore not readily obtained in characteristic crystals. It is important that the indium be present as sulphate and not as chloride or bromide, since the double chloride of cesium and indium is apt to be formed instead of the double sulphate. (See page 165.) In our experience the presence of a little free H_2SO_4 is desirable. These remarks relative to indium apply with equal force to gallium.

Although the "alum" test with cesium sulphate may lead to the separation of isotropic double sulphates of cesium other than those of the aluminum group, *e.g.*, those with chromium, manganese, titanium, thallium, and iron, there is no danger of confusion since all these salts are more or less colored and crystallize less readily.

It might be thought that a differentiation between the aluminum, gallium and indium cesium alums should be possible through a determination of their refractive indices; unfortunately this is not practicable, as will be seen by the following data:



The addition of Cs_2SO_4 to material of unknown composition, which has been prepared for analysis by treatment with H_2SO_4 , may give rise to the separation of anisotropic double sulphates mostly to be referred to the monoclinic system. When these salts appear, they are apt to puzzle the analyst; those most frequently encountered are the cesium double sulphates of magnesium, manganese, copper, zinc, cadmium, nickel, and cobalt. Fortunately, their solubilities are higher than those of the alums

and therefore they do not as a rule become troublesome, unless the concentration of salts in the test drop is too high or there has been too much H_2SO_4 used. They are usually so orientated upon the object slide that an extinction angle can be measured, and if this is done and the salt is not an isomorphous mixture, presumptive evidence of its component ions is possible.⁹

With bismuth an almost insoluble double sulphate is formed. (See Potassium, page 72; Bismuth, page 206.)

Because of the possibility of the formation of a variety of double sulphates it is essential that a moderately large fragment of Cs_2SO_4 shall always be added to the drop of solution to be tested.

The salt $\text{CsAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ has, under certain conditions, marked adsorptive powers and may separate distinctly colored and in modified crystal form; this source of error can be avoided by always following the method suggested above, *i.e.*, first precipitating the hydroxide of aluminum, washing and dissolving it in dilute H_2SO_4 .

Experiments.

(a) — To a test drop consisting of a solution $\text{Al}_2(\text{SO}_4)_3$ add a fragment of Cs_2SO_4 .

(b) — Precipitate another drop with NH_4OH , decant, wash the precipitate, dissolve in the least possible amount of H_2SO_4 and test.

(c) — Test for Al in the presence of free HCl.

(d) — Prepare slides of chrome alum, iron alum, etc., then mixtures of these various alums; note isomorphism.

(e) — Test preparations containing Al and Fe; Al and Cr; Al, Fe and Cr; Al in the presence of phosphates.

B—By Means of Ammonium Fluoride — NH_4F .

Compound Formed — $(\text{NH}_4)_3\text{AlF}_6$.

A large drop of a neutral or very slightly acid moderately concentrated solution of the aluminum salt is placed upon a celluloid or suitably coated object slide. A large fragment of NH_4F is introduced into the drop and the preparation allowed to stand undisturbed for a short time. There is first formed a granular or sandy precipitate which on standing becomes distinctly crystalline; soon tiny pseudo-octahedra, orthorhombic bipyramidal prisms or rectangular or rhombic plates appear¹⁰ (Fig. 93, page 137).

⁹ See Winchell: *Optic and Microscopic Characters of Artificial Minerals*, p. 81.

¹⁰ For the special precautions which are imperative when dealing with HF or its compounds, see p. 43.

The character of the precipitate varies with the concentration of the test drop with respect to Al^{+++} . If the crystals formed are atypical it is best to decant the mother liquor (using a platinum wire, never a glass rod) and recrystallize from hot water in which $(\text{NH}_4)_3\text{AlF}_6$ is readily soluble.

Instead of the ammonium salt the potassium salt K_3AlF_6 serves equally well for the identification of aluminum and the test may be thus modified. To the concentrated solution KCl is added and the drop stirred until all has dissolved. One or more drops of HF are added and the preparation allowed to stand, or the drop is acidified with HCl , the KCl added and then several fragments of NH_4F ; or KF may be added at once in place of NH_4F . RbCl or CsCl can be substituted for KCl . All these salts have a composition and habit similar to ammonium fluoaluminate and form an isomorphous series. These fluoaluminates are weakly birefringent and are so feebly refractive that great care must be used in properly adjusting the illumination.

The solution to be tested should be that of a relatively pure salt of aluminum or a solution obtained by dissolving in HCl a precipitate obtained with NH_4OH .

Indium and gallium fail to give the reaction when the test is performed as described above.

C—By Means of Cesium Chloride — CsCl .

Compounds Formed — $3 \text{CsCl} \cdot \text{InCl}_3 \cdot 2 \text{H}_2\text{O}$, or
 $2 \text{CsCl} \cdot \text{InCl}_3 \cdot \text{H}_2\text{O}$.

Precipitate with NH_4OH , wash the hydroxide and dissolve in HCl . To a moderately concentrated drop of solution thus prepared add a relatively large fragment of CsCl (or RbCl). In a few seconds highly refractive crystals of the double salt appear. These take the form of very thin rhombs, rhombic pyramids, and rectangular prisms (Fig. 98, page 159). This salt is extraordinarily birefringent and displays very brilliant polarization colors. This property together with a characteristic habit make the double chloride test an excellent one, providing that the test is performed on comparatively pure indium (*i.e.*, upon the HCl solution of the precipitated hydroxide), for CsCl forms readily crystallizable double chlorides with the chlorides of many elements. The separation of these double chlorides may mask or interfere with the test for indium.

Aluminum tested as above gives no crystalline compound unless the test drop passes to dryness, when a few anisotropic pseudocubic crystals may appear. If sulphates are present, aluminum alum may be precipitated.

Gallium yields a granular precipitate in which may be seen very tiny slender rods; later as the solution passes to dryness irregular anisotropic dendritic masses separate at the circumference of the drop.

Rubidium chloride may be substituted for CsCl.¹¹ The rubidium double salt is somewhat more soluble than the cesium double chloride and therefore forms larger and thicker crystals; in addition to the types described above, large well-formed octahedral-like crystals are obtained. These crystals are very strongly birefringent, but do not show the brilliant colors of the cesium salt. Aside from the crystals of octahedral aspect the double rubidium salt closely resembles the cesium salt in habit.

The stability of cesium indium chloride is so great that if chlorides are present in material being tested with Cs_2SO_4 , for the purpose of forming cesium indium sulphate, the former salt is apt to separate instead of the latter. A similar result follows in the case of testing with NH_4F , HCl , and CsCl by Method B, page 164; the double chloride is formed and not a fluoindate.

The formula of the cesium indium chloride appears to be in doubt. It is usually given as Cs_3InCl_6 or $3\text{CsCl}\cdot\text{InCl}_3$, but this salt appears to be tetragonal¹² while the salt $2\text{CsCl}\cdot\text{InCl}_3\cdot\text{H}_2\text{O}$ is orthorhombic. Under the conditions which obtain when the test is applied as above the salt that separates does not have a habit conforming to the tetragonal system. Moreover, the cesium salt behaves upon the object slide as if it were isomorphous with potassium indium chloride, whose formula is quite well established as being $2\text{KCl}\cdot\text{InCl}_3\cdot\text{H}_2\text{O}$. If the test drop is moderately concentrated with respect to indium, the crystals which separate are as described above, but if quite dilute or too concentrated other salts are formed.¹³

¹¹ Kley: *Chem. Ztg.* **25**, 563 (1901).

Behrens-Kley: *Mikrochem. Anal.* p. 82.

¹² Wallace: *Zeit. Kryst.* **49**, 417 (1911).

Pratt: *Amer. J. Sci.* (3) **49**, 397 (1895).

¹³ Investigations carried out by Chamot and Cole (1923) supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

D—By Means of Hexamethylenetetramine — $C_6H_{12}N_4$. — The hydroxides prepared as directed on page 161 are dissolved in HCl with the acid in slight excess. To the test drop thus prepared add the reagent by Method II, page 32. Indium yields tiny highly refractive isotropic octahedra (Fig. 99, page 159). Aluminum and gallium give no crystalline precipitates with $C_6H_{12}N_4$.¹⁴ (See page 363.)

DETECTION OF THALLIUM

The chief properties of thallium have been discussed on page 156 in relation to its position in Group III of the Periodic System. In aqueous solutions which have been boiled, thallic compounds are changed to thalrous salts, hence the analytical behavior of the latter alone need concern us.

A—By Means of Hydrochloric Acid — HCl.

Compound Formed — $TlCl$.

The method of procedure, characteristics and precautions relative to the identification by means of $TlCl$ have been discussed under Mercury, Method B, page 144. (See Fig. 101, page 169.) Confirm by treating the precipitate (1) with KI — no yellow hexagonal plates; (2) with H_2SO_4 — no conversion into an insoluble sulphate (distinction from lead).

B—By Means of Chloroplatinic Acid — H_2PtCl_6 .

Compound Formed — Tl_2PtCl_6 .

See Potassium, Method A, page 66. If a precipitate is obtained, confirm by testing a new portion of the substance with sodium iodide.

C—By Means of Sodium Iodide — NaI.

Compound Formed — TlI .

See Mercury, Method B, page 144; Method C, page 146.

D—By Means of the Triple Nitrite Reaction.

Compound Formed — $2 TlNO_2 \cdot Cu(NO_2)_2 \cdot Pb(NO_2)_2$.

For a discussion of this reaction and its application to the detection of thallium, see Lead, Method C, page 184.

¹⁴ Chamot and Cole, Heckscher Research Grant, 1923, *op. cit.* Martini: *Mikrochemie* 6, 28 (1928).

E-Miscellaneous Reactions of Thallium.

- (a)–Metallic zinc precipitates metallic thallium.
 - (b)–Not precipitated by alkali hydroxides or carbonates.
 - (c)–In dilute solutions no precipitate with H_2SO_4 .
 - (d)– K_2CrO_4 precipitates Tl_2CrO_4 , insoluble in dilute HNO_3 and in dilute H_2SO_4 .
 - (e)–TII is only very slightly soluble in excess of NaI or KI.
 - (f)– $\text{K}_4\text{Fe}(\text{CN})_6$ — yellow sandy precipitate.
 - (g)– $\text{Na}_3\text{Co}(\text{NO}_2)_6$ — fine granular or cubic precipitate.
 - (h)–Phosphomolybdic acid, fine yellow precipitate.
 - (i)– $(\text{NH}_4)_2\text{MoO}_4$, dense white granular precipitate, soon changing into moss-like masses and beautiful radiating clusters and sheaves of fine acicular crystals. Later hexagonal plates, six-pointed stars and six-pointed rosettes are formed.
 - (j)–Uranyl acetate gives tetragonal needles and prisms.
- (See Sodium, page 52. Fig. 100, page 169.)

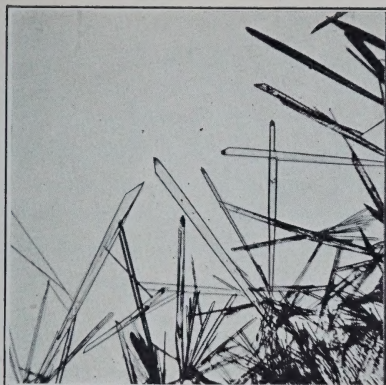


FIG. 100. Thallium (Tl^+) with Uranyl Acetate. 50 $\times$.

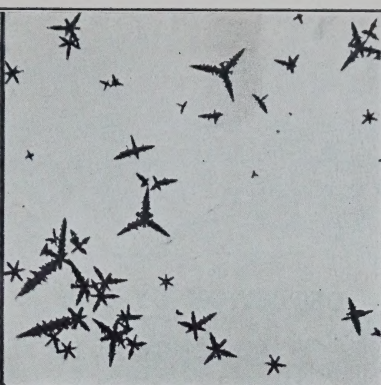


FIG. 101. Thallium (Tl^+) with Hydrochloric Acid. 100 $\times$.

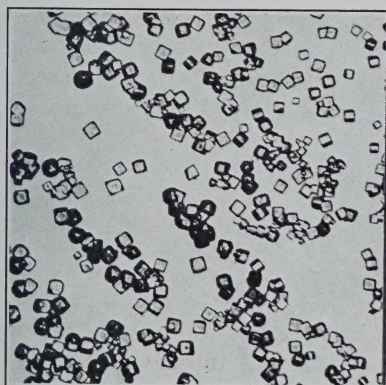


FIG. 102. Tin (Sn^{++++}) with Cesium Chloride. 200 $\times$.

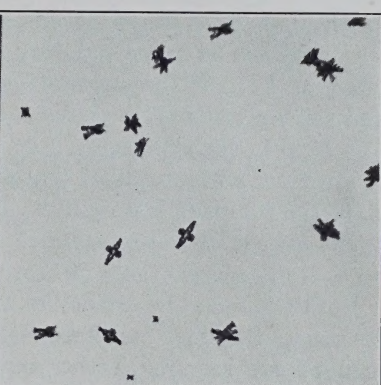


FIG. 103. Lead Sulphate Recrystallized from Conc. Sulphuric Acid. 300 $\times$.

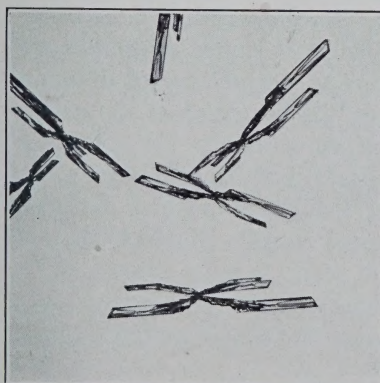


FIG. 104. Lead with Hydrochloric Acid. 100 $\times$.

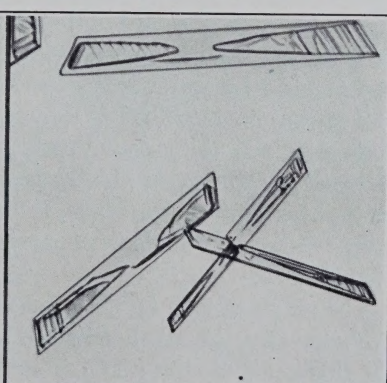


FIG. 105. Lead Chloride Recrystallized from Hot Water. 200 $\times$.

CHAPTER VI

DETECTION OF THE ELEMENTS OF GROUP IV

C; Ti, Zr, Hf, Th; Si, Ge, Sn, Pb

Group IV comprises the transitional element carbon; the primary vertical sub-group, titanium, zirconium, hafnium and thorium; and the secondary sub-group, silicon, germanium, tin and lead.

Carbon has no microanalytical relations with the other elements of Group IV. We have no satisfactory micro-reactions for carbon and we can test for its presence only indirectly through its oxide CO_2 fixed in carbonates.

Titanium and zirconium (hafnium) are closely related, not only as to the compounds they form but also in their behavior toward micro-analytical reagents; none of their "micro" reactions, however, are similar to those of thorium.

Both titanium and zirconium are acid-forming and we therefore encounter titanates and zirconates in materials whose qualitative analyses are required, rather than compounds in which titanium or zirconium function as cations; but the detection of the elements titanium and zirconium is required in alloys, pigments, refractories, and in minerals.

Titanium in HCl solution behaves somewhat like SnCl_4 but is more readily hydrolyzed on boiling. Zirconium being more basic, its salts are slightly more stable, but most simple zirconates are decomposed by water in the cold. The resemblance of titanium and zirconium to silicon is shown by the formation of the oxides TiO_2 and ZrO_2 , the ease with which they dissolve in HF , and their formation of the acids H_2TiF_6 and H_2ZrF_6 which closely resemble in their reactions the reactions of H_2SiF_6 . But their dioxides, unlike SiO_2 , are soluble in concentrated H_2SO_4 with the formation of sulphates.

The alkali salts of H_2TiF_6 and H_2SiF_6 are isomorphous, and it is probable that the alkali salts of H_2ZrF_6 are also isomorphous with the fluo-acids of silicon and titanium.

Solutions of the alkali titanates and zirconates are unstable, hydrolyze slowly on standing, and are decomposed on boiling.

For the detection of titanium, zirconium, silicon, and germanium, we are almost wholly dependent upon the formation of crystalline salts of the alkalis and alkaline earths with the fluo-acids of these elements.

A further analogy of titanium to silicon and to tin is the formation of titanate acid, H_4TiO_4 , and its readiness to form polyacids.

In both the vertical sub-groups of Group IV the basicity increases with the rise in atomic weight. Thus carbon and silicon at the top of the groups are strictly acid formers (metalloids), whereas in hafnium and thorium, and in tin and lead, the acidic properties are submerged in the strong basicity of these metals. Hafnium and thorium are better classed with the "rare earths," therefore their separations and detections are best discussed in connection with the other "rare earths." (See pages 280-285.)

The micro detection of silicon, like that of carbon, is impractical unless there is first conversion into its oxide, and subsequently the formation of an acid is induced. The ease with which SiO_2 is converted into H_2SiF_6 affords a simple and satisfactory test for silicon and silicates providing that titanium, zirconium, or germanium are absent.

Germanium reacts like silicon in forming fluogermanates, and like phosphorus and arsenic in forming volatile chlorides. A further resemblance to these elements is seen in the formation of complex molybdates.

Tin and lead have nothing in common micro-analytically, nor do they appear with any of the reaction products which serve to identify the other members of Group IV, save that tin forms crystalline fluostannates. (See page 65.) Their analogies are rather with adjacent elements in the horizontal periods but not with those above them. These analogies and differences hold true for all the heavy metals of highest atomic weight in the vertical columns of the eight groups of the Periodic System of the elements. Like these other elements of high atomic weight both tin and lead form two series of salts, "-ous" and "-ic."

Hafnium resembles zirconium so closely that it cannot at present be identified, nor differentiated from zirconium by micro-crystalline reactions. Thorium's reactions place it with the "rare earths."

DETECTION OF CARBON

Fragments of carbon (charcoal, coal, graphite) are opaque, black "amorphous," loose-textured or dense, light or heavy, not appreciably attacked by acids or alkalis, insoluble in organic solvents. Fragments burn when ignited and leave no perceptible ash. Heated to redness with KNO_3 or CuO in a tube or in a tiny crucible, CO_2 is formed, which can be fixed by a drop of a solution of alkali, or of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

The identification therefore turns on the recognition of carbonates. (See page 296.)

Graphite is usually met with as a dense heavy gray or black mineral or in the form of glistening micaceous scales often iridescent or brownish. Graphite is more resistant to ignition than amorphous carbon. Native graphite usually leaves a perceptible ash on ignition. It may be recognized by its refractory character, its appearance under the microscope, its physical properties, and the formation of CO_2 when burned in a current of oxygen. Pure graphite is not attracted by a magnet.

The identification of carbides (or of carbon thus combined) must depend upon the identification of the products of decomposition. Practically, each carbide constitutes a special case, and the plan of attack must be formulated in accordance with the chemical reactions which may be brought about with a variety of reagents. The problem is difficult of solution. No methods of general applicability are possible.

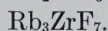
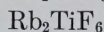
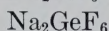
Carbon in "organic" compounds can be detected by burning in a tiny combustion apparatus such as that of Emich or Pregl.¹

DETECTION OF SILICON, GERMANIUM, TITANIUM
AND ZIRCONIUM

With the exception of zirconium the micro-reactions of this group of elements are so nearly identical that their differentiation on a "micro" scale is often impracticable.

The hope of positive identification must be based upon separation methods before an identity test can be successfully applied. Some of the separation methods which offer a possible chance of success are discussed below, following the special reactions.

¹ Emich: *Mikrochemisches Praktikum* (Bergmann, München, 1931). Pregl: *Die quant. organ. Mikroanalyse* (Springer, Berlin, 1930).

A—Conversion into Alkali Salts of Fluo-acids — H_2RF_6 .*Compounds Formed* — Na_2SiF_6 

Use a celluloid, cellulose acetate or other non-siliceous, transparent, object slide and observe all the precautions given on page 43.

To a concentrated drop somewhat larger than is usually employed in microchemical analysis add a tiny droplet of dilute H_2SO_4 , then a fragment of $NaCl$. Stir with a platinum wire and add a large fragment of resublimed NH_4F . Warm the preparation by laying it upon a warm metal surface. (See Fig. 1, page 5.) Allow to stand for a few minutes until thoroughly cold and crystals have begun to form.

Warming the preparation is not essential, but is nevertheless always advisable, for it hastens the reaction and seems to prevent the formation of $NaHF_2$. This acid fluoride of sodium crystallizes in hexagonal plates and rosettes, but its refractive index is higher than that of Na_2SiF_6 .²

All four elements yield rosettes, six-sided plates, skeletons of hexagons, perfect hexagons, and six-sided prisms with square ends or terminating in pyramids (hexagonal system). Their indices of refraction are all so very low that they are almost invisible ($n = 1.31+$; water $n = 1.33+$). Their birefringence is also very low.

Na_2SiF_6 and Na_2GeF_6 are of sufficiently low solubility to separate before the test drop has evaporated to dryness; the colorless crystals appear pink under the microscope (Christiansen effect), and separate first at the circumference of the drop. (See Sodium, page 63.) K_2SiF_6 is quite soluble but K_2GeF_6 is very difficultly soluble.

The solubilities of Na_2TiF_6 and Na_2ZrF_6 are too great for these salts to separate unless the concentration is very high and the test drop is about to pass to dryness.

Since the silicon and the germanium salts have a sufficiently low solubility to appear in crystal form after the preparation has stood several minutes, the non-appearance of pink hexagons indicates the absence of silicon and germanium. To the preparation there

² Mellor: *op. cit.*, II, p. 516.

can then be added RbCl ; if titanium is present, thin, square and rectangular plates with truncated corners, rhombs and six-sided plates (not regular hexagons) of the compound $\text{Rb}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ are obtained.

Zirconium gives highly refractive, strongly birefringent, well-formed octahedra which have the formula $3\text{RbF} \cdot \text{ZrF}_4$, according to Behrens.³

With boron the salt Na_2BF_6 (?) is obtained, of identical habit with Na_2SiF_6 .

The fact that the fluoborate usually does not show the Christiansen effect is not sufficient ground for differentiation. The specific test for boron with turmeric-viscose-rayon fibers must always be made. (See Boron, page 156.) Titanium gives a brown color and zirconium a reddish-brown or pink, but only with boron is the fiber turned blue with KOH . Thorium gives no color.

Since silicon and germanium are readily separated from titanium and zirconium, the NH_4F , or better the KF , test can be made to yield dependable results since potassium fluogermanate is very difficultly soluble, but if applied to material directly, the reaction becomes a general one, to be regarded merely as an indication of a group of closely related anion-forming elements. (See Figs. 35, 36, page 61; Fig. 93, page 137; Figs. 94, 95, 96, 97, page 159.)

B-Conversion into Complex Molybdates. — The material to be tested is treated upon platinum foil or in a platinum cup in the manner described below. After the final treatment and evaporation to dryness on platinum the residue is dissolved in pure water and a fragment of ammonium molybdate is added. The mixture is next heated to boiling to assure the formation of the necessary complex molybdates. Evaporate again almost to dryness, treat with HNO_3 and once more evaporate. Dissolve the residue in a drop or two of pure water and transfer the very dilute solution to a celluloid object slide. Add to the *clear* solution a fragment of RbCl .

Rubidium silicomolybdate or rubidium germanomolybdate is formed. Both these compounds separate with identical habit —

³ *Anleitung*, p. 90; but to the potassium salt he ascribes the formula $2\text{KF} \cdot \text{ZrF}_4$.

tiny, isotropic, yellow, spherical crystals or octahedra and dodecahedra⁴ (Fig. 46, page 81).

Freshly distilled water should be employed, not water that has stood for a long time in glass.

It is obvious that evaporation cannot be performed on glass or quartz object slides, nor in glass, quartz or porcelain vessels, nor can the final observations be made upon a glass or silica object slide unless protected by a suitable varnish.

The test is sensitive to very minute amounts of silicon or germanium, hence it is essential that a "blank" be carried out with all the materials employed.

Somewhat better crystals of rubidium silico- or germano-molybdate can usually be obtained by applying the tests as suggested under rubidium and cesium.

If rubidium and cesium (and Tl+) are absent and a very fine yellow precipitate appears on heating a test drop of a water solution with $(\text{NH}_4)_5\text{H}_7(\text{MoO}_4)_6$ in HNO_3 , phosphorus or arsenic are probably present (*i.e.*, ammonium phospho-molybdate or ammonium arseno-molybdate has separated). But unless the concentration of the drop has been made too great, neither silico-molybdates nor germano-molybdates will separate until the rubidium salt has been added. Even the potassium salt of these two complex acids will not separate from dilute solutions. Behrens has pointed out that advantage can be taken of this fact to differentiate between silicon (and Ge) and vanadium, columbium, tantalum, and bismuth.⁵ Thorium forms a complex molybdate rubidium salt not distinguishable from the silicon compound.

Germanium is separated from silicon and other interfering elements by conversion into GeCl_4 with concentrated HCl and distillation. GeCl_4 distils at 86°C .⁶ The material to be tested is introduced into the crucible of the micro-distillation apparatus illustrated on page 15 and described in *Vol. I*, page 352. If the material is a neutral solution, evaporate to dryness. Several drops of concentrated HCl are added and a few fibers of ignited asbestos introduced to guard against splashing. Cover the crucible with a celluloid object slide and heat gently over a micro-burner until vapors begin to condense upon the slide; allow to stand a few

⁴ For a further discussion of this and analogous salts see p. 80.

⁵ Behrens: *Anleit. mikrochem. Anal.* p. 95.

⁶ Dennis and Hance: *Jour. Amer. Chem. Soc.* **44**, 305 (1922).

seconds and heat again. Repeat the process several times until the condensate upon the slide is as large in amount as the slide will carry. Remove the slide, replace it by a fresh one and distil again. Unite all the distillates, transfer to a platinum cup or foil, acidify with HNO_3 , add $(\text{NH}_4)_5\text{H}_7(\text{MoO}_4)_6$, and proceed as above. Germanium cannot, however, be separated from SiO_2 insoluble residues by distillation.

Arsenic may have passed over with the germanium, therefore it is wise to test the distillate with NH_4F and KCl as well as with $(\text{NH}_4)_5\text{H}_7(\text{MoO}_4)_6$ and RbCl .

In order to eliminate as far as possible such other elements as may give products similar to rubidium silicomolybdate it is best to separate the silicon from the other material. Fuse the material in a platinum cup with several times its weight of Na_2CO_3 . Dissolve in HCl , evaporate to dryness, and heat the residue (but not above 110°C). Moisten with concentrated HCl and heat again; repeat the process so as to render the SiO_2 insoluble. Extract the residue repeatedly with dilute HCl , filtering if necessary to avoid loss of SiO_2 . Dry the SiO_2 and fuse with Na_2CO_3 . Dissolve in water, add the molybdate, and proceed as directed above.

The residue of insoluble SiO_2 may contain germanium, titanium, columbium, tantalum, and adsorbed traces of other oxides. The absence of molybdate-forming elements must always be proved before the presence of silicon can be considered as assured. Checks should be made by carefully volatilizing the silicon as SiF_4 and testing the residue with KF .

C-Staining Methods. — The hydrous oxide of silicon precipitated by HCl from a water-soluble silicate takes up certain dyes with great avidity.

Staining with malachite green, methylene blue, or aniline blue is useful when dealing with pure hydrated SiO_2 but is of little value if the hydrous oxide is impure. Staining gives no information relative to the impurities present.

D-By Means of Ammonium Thiocyanate and Quinoline.⁷ — To the moderately concentrated acid solution containing titanium or zirconium an alcoholic solution of NH_4SCN containing a moderate amount of quinoline is added by Method I.

⁷ Martini: *Trabajos al Segundo Cong. de Quimica, Buenos Aires, 1924*, p. 67.

Zirconium forms bundles of colorless feathery crystals of a complex salt of uncertain composition.

Titanium forms orange-yellow monoclinic prisms.

According to Martini the best results are obtained when the zirconium is in HNO_3 solution and the titanium in HCl solution. Dependable results are obtainable only after long experience, for it is difficult properly to adjust concentrations.

This method is not applicable to mixtures of unknown composition.

E-Miscellaneous Reactions.

(a)-Cold concentrated K_2SO_4 precipitates a complex zirconium sulphate, insoluble in excess. (Distinction from Be, Al, Ti.) This salt is soluble in HCl , but if the solution is boiled a basic salt is precipitated, insoluble in excess of HCl .

(b)-Solutions containing titanium give a blue or violet color with Zn and HCl . Vanadium gives a blue, then green and finally violet.

(c)-Hydrogen peroxide gives an orange color with titanium salts in acid solution if the concentration of Ti is high, yellow if low. V, Ce, Cb, Ta, also give yellow colors of various hues.

DETECTION OF TIN

A-By Means of Cesium Chloride — CsCl .

Compound Formed — Cs_2SnCl_6 .

The tin must be in solution as stannic chloride, SnCl_4 , in HCl ; *i.e.*, as chlorostannic acid, H_2SnCl_6 . To this very dilute solution to be tested a solution of CsCl is added by Method I, page 30.

The very tiny colorless octahedral or cubical crystals of Cs_2SnCl_6 which are formed are so small that unless an exceedingly dilute test drop is used, their true habit is not readily perceived (Fig. 43, page 67, Fig. 102, page 169). Their appearance and chemical characteristics have been discussed under rubidium and cesium, page 82, and as there described, advantage can be taken of the formation of the iodo-salt to render the crystals more prominent and increase the sensitivity of the reaction.

For reasons given below it is generally essential to separate the tin from other heavy metals before applying the CsCl reagent. The separation is most easily accomplished by converting the tin

into insoluble metastannic acid. Treat the material to be tested with several drops of strong HNO_3 (sp. gr. 1.20) and carefully evaporate to dryness. Repeat the process again and again until all the tin has been thrown out of solution as SnO_2 . Extract thoroughly with HNO_3 and dissolve the residue in aqua regia. Drive off the excess of acid, take a small portion, dilute well, and test with CsCl .

Any antimony which may be present in the material under examination will appear in the residue of SnO_2 as Sb_2O_4 . Arsenic may also have been precipitated by the HNO_3 as As_2O_3 . The extraction with HNO_3 will seldom remove all the Sb_2O_4 .

The extraction with boiling HNO_3 must be very thoroughly done, since metastannic acid has great adsorptive properties and carries down with it material which may react with CsCl , *e.g.*, copper, iron, lead, antimony, bismuth, etc.

CsCl forms double salts with a large number of other chlorides. Many of these double chlorides are characterized by their stability and the ease with which they crystallize. These salts may separate (if present) in the test for tin and interfere with or mask the identity reaction. A discussion of these salts will be found on pages 136-141.

Cesium cadmium chloride, $\text{CsCl}\cdot\text{CdCl}_2$, separates in hexagonal bipyramidal twins which when very small may be mistaken for octahedra. They are, however, anisotropic.

If silver is present, and is not eliminated by the above treatment, tiny octahedra of AgCl will be formed.

An additional reason for always converting tin into metastannic acid and extracting all soluble material is to avoid error through the formation of "alums." If much SO_4^{--} is present and any alum-forming element, the addition of a cesium salt may be followed by the separation of octahedral crystals. The cesium alums are, however, so very much more soluble than Cs_2SnCl_6 that the octahedra of the alums grow much larger and are readily soluble in warm water, whereas cesium chlorostannate is always in very tiny crystals almost insoluble in warm water.

If phosphorus or phosphates are present the metastannic acid will carry down with it most, if not all, of these substances, and subsequent tests will fail to detect them in the HNO_3 solution which has been decanted from the metastannic acid.

Experiments.

- (a) — Test dilute and concentrated solutions of tin.
(b) — Test for tin in an alloy.

B—Recognition of Stannous Salts.

1—Identify tin by CsCl before proceeding to test for Sn^{++} (Test A, page 177).

2—Stannous salts give with oxalic acid or alkali oxalates, stannous oxalate, $\text{Sn}(\text{C}_2\text{O}_4)$, separating in a great variety of prismatic or imperfectly developed crystals, mostly skeletal or dendritic forms, somewhat X-shaped but quite irregular. When elongated into prisms with a roof-like configuration the crystals exhibit parallel extinction but, as shown by Haushofer, characteristic twinning can be observed in which the extinction angle is 14° to 15° with the direction of elongation. These twins are usually thin plates with two parallel sides and irregular reëntrant ends. It is probable that stannous oxalate is monoclinic (Fig. 68, page 109).

Stannic salts give no reaction with oxalic acid.

Stannous salts give a yellowish white precipitate with KI, and if an excess of KI is added, a double salt is formed, separating in orange acicular crystals. Stannic salts yield at once a yellow precipitate.

3—Stannous salts, especially SnCl_2 , reduce chloroauric acid with the formation of colloidal gold.

We can therefore identify SnCl_2 by using HAuCl_4 as a reagent and applying Cole's viscose-rayon test for gold.⁸

Evaporate to dryness the solution to be tested; dissolve in several large drops of water acidulated with HCl. Decant or filter. To the clear solution add an amount of pyrogallol about equal to the weight of SnCl_2 probably present. Immerse in the drop a fiber of viscose-rayon about 5 mm. long. Warm gently and allow to evaporate to dryness. Dissolve the whole mass in water, warm, and evaporate again. Introduce the fiber into a tiny drop of moderately dilute HAuCl_4 , following the suggestions given in Method VI, page 37.

If SnCl_2 is present that part of the fiber in the liquid will turn red, purple, or blue.

This test, though an excellent and exceedingly sensitive reaction for gold (See page 278), is not wholly dependable when applied in

⁸ Cole, H. I.: *Philippine Jour. Sci.* **21**, 361 (1922).

modified form for Sn^{++} , since it is difficult to prevent almost complete oxidation where only small amounts of tin are present.

DETECTION OF LEAD

A—By Means of Potassium Iodide — KI.

Compound Formed — PbI_2 .

The reagent is applied by Method I, page 30, to the not too dilute test drop previously acidified with HNO_3 .

Lead iodide — PbI_2 — separates at once in bright yellow thin scales and hexagonal plates (Fig. 106, page 181), that appear to be greenish, brownish or even gray by transmitted light. By reflected light the plates and scales scintillate and glisten with iridescent colors as they turn over in the solution (colors of thin films) — a characteristic that is peculiar to yellow hexagonal plates of PbI_2 . Lead iodide is soluble in a *large excess* of KI, the double salt $\text{PbI}_2 \cdot \text{KI} \cdot 2 \text{H}_2\text{O}$ being formed. Too much HNO_3 will cause a decomposition of the PbI_2 with the formation of $\text{Pb}(\text{NO}_3)_2$, and this being a salt of low solubility it will separate in the form of isotropic highly refractive colorless octahedra. The appearance of clear, colorless, octahedral crystals under these conditions should be considered indicative of the presence of lead since only barium, and arsenic give isotropic regular octahedra separating in a test drop acidulated with HNO_3 .

PbI_2 is moderately soluble in hot water, from which on cooling it again separates in large beautifully formed hexagons. To obtain the best results a large drop of water acidified with HNO_3 is essential.

Lead forms double iodides with many elements.⁹ Most of these double salts crystallize well, but their solubilities are sufficiently great to keep them in solution until the test drop passes almost to dryness.

From neutral solutions, especially those of lead salts of organic acids, basic iodides are apt to form, such as $\text{PbI}_2 \cdot \text{PbO}$; $\text{PbI}_2 \cdot 2 \text{PbO}$ and others, all of uncertain composition. These basic salts may interfere with or obscure the formation of the normal salt.

Heated with HCl , the PbI_2 is dissolved, and upon cooling crystals of the normal iodide PbI_2 , normal chloride PbCl_2 , and chloriodides $\text{PbCl}_2 \cdot \text{PbI}_2$ and $2 \text{PbCl}_2 \cdot \text{PbI}_2$ separate. The chloriodides appear as acicular crystals having a faint yellow color.

⁹ Mosnier: *Ann. Chim. Phys.* (7) **12**, 374 (1897).

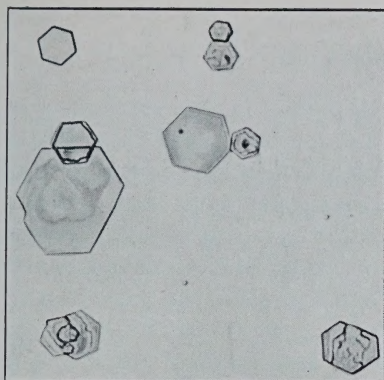


FIG. 106. Lead with Potassium Iodide. 100 $\times$.

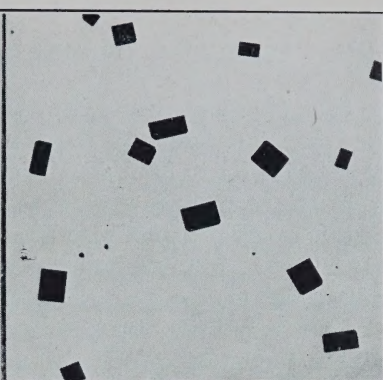


FIG. 107. Lead with Potassium Nitrite and Copper Acetate. 100 $\times$.

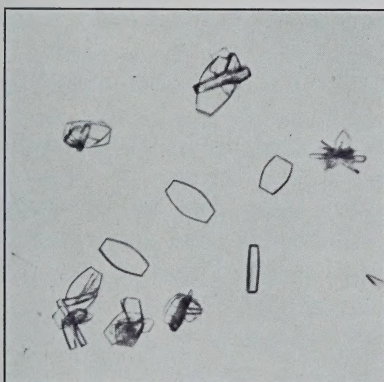


FIG. 108. Vanadium Precipitated as Ammonium Metavanadate. 400 $\times$.

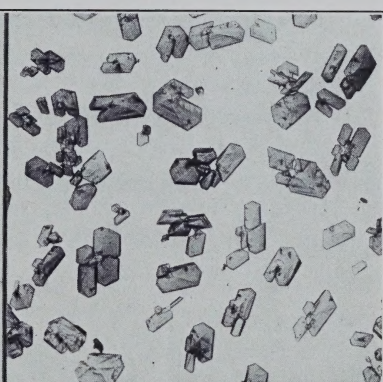


FIG. 109. Ammonium Metavanadate Recrystallized from Acetic Acid. 100 $\times$.

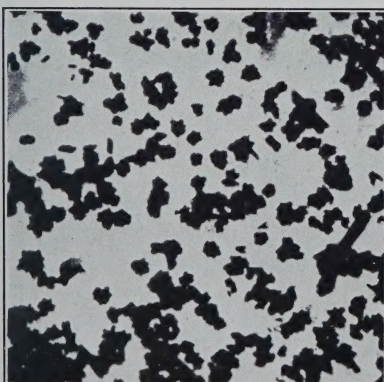


FIG. 110. Vanadium Precipitated as Silver Pyrovanadate. 400 $\times$.

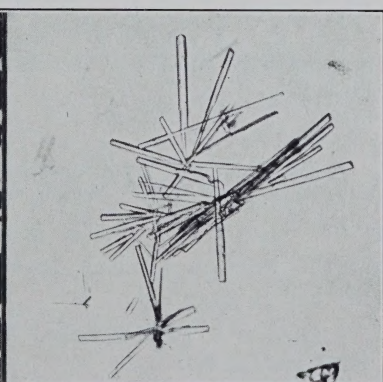


FIG. 111. Tantalum with Potassium Fluoride. 100 $\times$.

Salts of antimony and bismuth, if present in moderate amounts, seriously interfere with the KI test for lead, since they readily unite with KI to form double iodides, and in the presence of lead complex compounds are formed that separate as dark reddish-brown sandy precipitates. Boiling the test drop, slightly acidified with HNO_3 , will usually cause a decomposition of these complex salts, and on cooling typical crystals of PbI_2 can be obtained. Even a very little bismuth may (if the conditions are right) lead to the formation of orange-red disks and irregular plates having no resemblance to PbI_2 .

In the event of evidence being obtained of the possible presence of antimony or bismuth, proceed as follows: to a very dilute solution add a very little dilute H_2SO_4 , filter or centrifuge and test the precipitate with KI.

For a discussion of the other elements that are precipitated by KI, see Mercury, page 146.

If lead, only, is to be tested for, it is generally better to add the KI by Method II, page 32.

According to Groth¹⁰ PbI_2 is to be referred to the hexagonal system. PbCl_2 and PbBr_2 are orthorhombic and form isomorphous mixtures with each other but not with PbI_2 .

Experiments.

(a) — To a test drop containing $\text{Pb}(\text{NO}_3)_2$ add KI. Study the preparation, then add a drop of water and heat to boiling. After the drop has cooled, study it again. Repeat the experiment, but this time use an excess of KI. Try again in acidified solution.

(b) — Make a preparation of PbSO_4 . Decant the mother liquor, add to the sulphate residue a drop of water, acidify with HNO_3 , then add a fragment of KI. After a few seconds examine the preparation.

(c) — Make a mixture of Pb and Ag; test with KI. Then try in turn mixtures of Pb and Sb; Pb and Bi; Sb and Bi; Pb and Cu; Pb and Sn; Pb and Hg.

B—By Means of Hydrochloric Acid — HCl .

Compound Formed — PbCl_2 .

The method of applying the reagent and the general properties of the reaction product have been discussed under Mercury, Method B, page 144.

¹⁰ *Elemente d. Phys. u. Chem. Krystallographie* (Oldenbourg, München, 1921), pp. 275, 306.

Since PbCl_2 is quite soluble in hot water the test drop should be cold before the reagent is added; it is also essential that the test drop shall be moderately concentrated and slightly acidified with HNO_3 . In strictly neutral solutions of lead acetate containing elements of Group I, the addition of HCl (if not in excess) may cause the precipitation of colorless, highly refractive ($n = 2.08+$) orthorhombic prisms believed to have the formula $\text{Pb}(\text{OH})\text{Cl}$; but sometimes monoclinic prisms are formed.

Too much HNO_3 may lead to the separation of glittering octahedra of $\text{Pb}(\text{NO}_3)_2$, for this salt is of low solubility and almost insoluble in HNO_3 .

PbCl_2 is more soluble in water acidified with HNO_3 than in pure water, hence the precipitation of the lead is never complete. It is differentiated from the chlorides of Ag^+ and Hg^+ by its solubility in hot water. On cooling there are obtained pseudo-hexagonal plates, prisms, and rhombs. The thin six-sided prisms are especially characteristic and can be seen to be the fully developed crystals, of which the X-shaped crystals, in the cold, are skeletons (Figs. 104, 105, page 169).

PbCl_2 forms with chlorides of the elements of Group I a large number of readily soluble double chlorides, all of them with habits very different from that of the normal chloride. It is quite important that the analyst shall be familiar with at least the double cesium salt — cesium chloroplumbate — since crystals of this compound are not infrequently obtained when CsCl is used in testing for cadmium, tin, antimony, and bismuth. Cesium chloroplumbate $4 \text{CsCl} \cdot \text{PbCl}_2$ usually separates in rhombohedral tablets, but when they are small and thin they appear to be square and rectangular plates with parallel extinction.

For the appearance and characteristics of HgCl , AgCl , TlCl , see page 144.

Experiments.

(a) — To a drop of a concentrated solution of $\text{Pb}(\text{NO}_3)_2$ add a drop of dilute HCl in the manner described above. Make several other preparations, varying the concentrations of the test drops.

(b) — Recrystallize a preparation of PbCl_2 by heating to boiling with a large drop of water.

(c) — Precipitate PbCl_2 in the presence of an alkali chloride.

C—By Means of the Triple Nitrite Reaction.

Compound Formed — $2 \text{KNO}_2 \cdot \text{Cu}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$.

Since it is essential that the test drop be as concentrated as possible it is simplest to adopt the procedure of Schoorl¹¹ and evaporate the solution to dryness. The dry residue is covered with a small drop of moderately concentrated acetic acid, a fragment of $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$ is added and when all is dissolved a large fragment of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ ¹² is added and allowed to dissolve. Finally a fragment of KNO_2 is introduced at the center of the drop and the preparation is allowed to stand for a few seconds.

If lead is present there will be formed a triple nitrite of potassium, copper, and lead. This salt separates in tiny isotropic square and rectangular plates, and in cubes and rectangular prisms which unless very thin are jet black by transmitted light but appear brownish by reflected light (Fig. 107, page 181). Thin plates and prisms may be brown or orange colored by transmitted light. On standing these crystals thicken and become black.

Although the reaction requires a slight excess of KNO_2 , too great an excess must be carefully avoided since the triple nitrite is soluble in the presence of an excess of KNO_2 .

In the salt $2 \text{KNO}_2 \cdot \text{Cu}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$, potassium may be replaced by rubidium, cesium, or thallium, the solubility decreasing in the order named. The sensitivity of this reaction for lead may be apparently increased by introducing into the test drop cesium or thallium. Nickel and mercury can replace copper, and strontium and barium can replace lead.

With nickel the salt formed is believed to have the formula $2 \text{KNO}_2 \cdot \text{Ni}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$. This salt also crystallizes in square and rectangular plates and in cubes and rectangular prisms; *i.e.*, with a habit similar to that of the copper salt, but the crystals are much smaller and are yellowish-brown in color, never black.

Cobalt forms with members of the potassium group, and with NH_4^+ , a very difficultly soluble double nitrite, $3 R \text{NO}_2 \cdot \text{Co}(\text{NO}_2)_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$, which immediately separates as an exceedingly fine, granular, faintly reddish-brown precipitate, or more rarely, as very tiny cubes and regular octahedra. The corresponding nickel double nitrite is much more soluble and appears as tiny yellow

¹¹ *Beiträge z. mikrochem. Anal.* (Wiesbaden, 1909), p. 22.

¹² Mayrhofer: *Mikrochem. d. Arzneimittel u. Gifte*, p. 134, has shown that to obtain the best results the ratio of copper to lead should be about 10 : 1.

four-sided plates and tables, or as yellow cubes and rectangular tablets, but these crystals are never black. In the presence of cobalt the test for lead or copper will usually fail because of the formation of the difficultly soluble potassium cobaltinitrite. It is then essential to decant after the cobalt has been precipitated, concentrate the decanted solution and add more nitrite; but even under these conditions the results are not satisfactory.

Rhodium is precipitated as $3\text{KNO}_2\cdot\text{Rh}(\text{NO}_2)_3$ in spheres and yellow cubes which cannot readily be distinguished from those formed by cobalt (Fig. 132, page 247). Palladium forms long thin curving lemon-yellow prisms as the test drop passes to dryness. The other members of the platinum group do not interfere with the precipitation of cobalt.

The triple nitrite reaction can be used to advantage in testing for copper by omitting the copper acetate and proceeding otherwise as directed. This reaction is especially useful in testing material thought to contain both lead and copper, as it is capable of yielding results more rapidly than other available methods. In such cases the dry material is covered with acetic acid, sodium acetate is added, then the KNO_2 . If no black cubes appear add a little CsCl in order to increase the sensitivity of the reaction. The appearance of black cubes points to the presence of both lead (or barium) and copper. In the presence of copper the reaction for nickel is masked by the deep black copper salt.

Unlike most micro-reactions the test drop may be allowed to pass to dryness, before the final observations are made. The jet-black crystals are usually readily discovered amidst the confused mass of other crystalline substances.

The substitution of NaNO_2 for KNO_2 and the introduction of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ as well as $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ into the test drop convert the triple nitrite reaction into an excellent test for K^+ (or members of the potassium group). The size of the black cubes affords a possible though very uncertain means of distinguishing between K^+ , Rb^+ , Cs^+ , and Tl^+ since the potassium triple salt grows largest and the Tl^+ smallest.

The triple nitrite reaction may be brought about in a variety of ways in the testing of material of unknown composition. The following outline may serve as an indication of some of its manifold uses. In all the examples cited, it is assumed that the solution to be tested has been evaporated to dryness, that a drop of

acetic acid and a fragment of sodium acetate have been added to the dry residue before the application of the nitrite.

I—Add a fragment of pure NaNO_2 .¹³

- (a)—An exceedingly fine reddish-brown precipitate is formed:
Co and either K, Rb, Cs, Tl or NH_4 .
- (b)—Black plates and cubes:
Cu and Pb plus K, Rb, Cs, Tl, NH_4 ; or Cu and Ba plus K, Rb, Cs, Tl, NH_4 .
- (c)—White granular precipitate:
Pb and Hg plus K, Rb, Cs, Tl, NH_4 .

II—No precipitate was obtained in I. Add KNO_2 .

- (d)—A fine reddish or yellowish precipitate is formed:
Co or Rh.
- (e)—Yellow plates and cubes:
Ni and Pb (Co, Rh).
- (f)—Black plates and cubes:
Pb and Cu, or Sr and Cu, or Ba and Cu, or mixtures (Ni, Co).
- (g)—White granular precipitate:
Pb and Hg, or Sr and Hg, or Ba and Hg or mixtures.

III—No test was obtained in II. Add $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.

- (h)—Black plates and cubes:
Pb (Sr, Ba).

IV—No test was obtained in III. Prepare a fresh film of the original material, add a fragment of $\text{Pb}(\text{C}_3\text{H}_2\text{O}_2)_2$, then add $\text{HC}_2\text{H}_3\text{O}_2$, $\text{NaC}_2\text{H}_3\text{O}_2$, and finally KNO_2 .

- (i)—Black plates and cubes:
Cu (Ni).
- (j)—Yellow plates and cubes:
Ni, Co, or Rh, or mixtures.

¹³ The NaNO_2 must be free from potassium. Since most NaNO_2 of commerce contains potassium it is always necessary to make a "blank" test with cobalt acetate in order to be sure of the purity of the reagents. For a method for the purification of sodium nitrite see Noyes and Bray: *Qual. Anal. Rare Elements*, p. 486.

Note. The addition of NaNO_2 or KNO_2 may lead to the separation of AgNO_2 in long slender greenish yellow needles or prisms.

The addition of $\text{NaC}_2\text{H}_3\text{O}_2$ or $\text{HC}_2\text{H}_3\text{O}_2$ may cause a separation of $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$.

Under exceptional conditions $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)$ may be formed.

Experiments.

- (a) — Test a preparation containing Pb by the triple nitrite reaction.
- (b) — Try another preparation, this time introducing Cs.
- (c) — By a series of careful dilutions determine the limit of the precipitation of Pb as the K salt, the Cs salt, and the Tl salt.
- (d) — Test a mixture of Pb and Ni; Pb and Co; Pb and Ag.

D—By Means of Sulphuric Acid — H_2SO_4 .

Compound Formed — PbSO_4 .

The formation and the properties of PbSO_4 have been discussed under the H_2SO_4 reactions of the Alkaline Earths. (See page 96.)

PbSO_4 separates as a fine granular precipitate. Decant, wash and test as below.

Boil with HNO_3 ; rectangular plates and rhombs separate on cooling. In rare cases octahedra of $\text{Pb}(\text{NO}_3)_2$ may be obtained.

Heat with concentrated H_2SO_4 until white fumes are evolved. Cool and breathe upon the drop. Spindle-shaped crystals and irregular skeletal or dendritic crystals or aggregates are obtained (Fig. 103, page 169).

Treat with KI. PbI_2 is formed.

PbSO_4 is soluble in $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$.

Other Reactions of Lead.

- (a) — With oxalic acid, see page 105 (Alkaline Earths).
- (b) — With potassium or ammonium bichromate; see page 252 (Silver).
- (c) — With sodium bicarbonate; see page 132 (Zinc).
- (d) — With alkali tartrates; see page 72 (Potassium).
- (e) — With potassium antimonyl tartrate; see page 208 (Antimony).
- (f) — With nitric acid. $\text{Pb}(\text{NO}_3)_2$ is difficultly soluble in HNO_3 and may therefore separate when this acid is used as a solvent. $\text{Pb}(\text{NO}_3)_2$ forms colorless, highly refractive isotropic octahedra.

General Method for "Opening Up" the Material, in Testing for the Elements of Groups IV and V. — The finely powdered material is fused in a platinum cup with about five times its volume of sodium pyrosulphate.¹⁴ The fusion should be carried out at a temperature below the driving off of SO_3 .

Dissolve in hot water, acidifying with H_2SO_4 . The insoluble residue may contain Si, Ge, Cb, Ta, Ba, Sr, Ca, Pb, Ti, Zr, Fe, Sn, and W.

For methods for the removal of Ba, Sr, Ca, and Pb see the Alkaline Earths, page 104; and Lead, page 180.

Fuse the residue with NaOH, dissolve in cold water; filter. Sodium silicate is soluble, but sodium columbate and sodium tantalate are relatively insoluble in NaOH.

To the NaOH solution add HCl to precipitate the silica; filter; wash; dissolve part of the SiO_2 in HF or $\text{NH}_4\text{F} + \text{HCl}$ on a celluloid or cellulose acetate slide, and add NaCl.

To another part of the precipitated "silica" add HF and heat to drive off SiF_4 . Repeat the treatment several times until the residue no longer diminishes in amount. Test the residue for Ti and Zr.

The above separation method is in no case quantitative, and the results obtained must be interpreted with great care.

¹⁴ Putnam, Roberts, and Selchow: *Amer. Jour. Sci.* **15**, 101 (1928). The reagent is prepared by heating pure HNaSO_4 in a platinum crucible, until all water has been expelled and fumes of SO_3 begin to rise. Cool, pulverize, and keep in a sealed bottle.

CHAPTER VII

DETECTION OF THE ELEMENTS OF GROUP V

N; V, Cb, Ta; P, As, Sb, Bi

In Group V the transitional element nitrogen affords practically no micro-reactions that correlate it with the other members of the group.

The sub-group containing vanadium, columbium, and tantalum is closely related to silicon, titanium, zirconium, germanium, and tin; like these elements vanadium, columbium, and tantalum are acidic, and salts in which they function as cations are rarely, if ever, encountered in routine qualitative analyses. Save in the case of some of the newer alloys the only compounds normally met with are vanadates, columbates and tantalates. But the resemblances are not alone with Group IV, for we find in certain reactions of analytical importance a close analogy exists with chromium, molybdenum and tungsten of Group VI; the analogies are especially true as regards the element vanadium, but to a less degree for columbium and tantalum. There is also a somewhat closer relationship between the two sub-groups of Group V than is shown by the sub-groups of the other vertical groups of the periodic system. This is shown by the isomorphism of the ortho-vanadates with the orthophosphates and orthoarsenates. So too we have metavanadates and metaphosphates behaving similarly. Moreover, as we have alkali silicomolybdates and tungstates, so we find alkali vanado-, phospho-, and arseno-molybdates and tungstates, all soluble in water.

Columbium and tantalum resemble titanium and zirconium more closely in their analytical behavior than they do the other elements of Groups IV and V. These two elements are so closely related that in most cases their microscopic differentiation is impracticable, particularly when small amounts of material only are available; for their micro-reactions are based mainly upon the relative solubilities of reaction products rather than upon crystal habit, hence positive identification is exceptionally difficult.

Most of the salts containing phosphorus with which we have to deal are isomorphous with those containing arsenic; nevertheless, the micro-differentiation of these two elements is not at all difficult. Like the elements of the first sub-group, phosphorus and arsenic function chiefly as anions. The transition from these acidic elements to the basic elements antimony and bismuth is very marked, nevertheless antimony and arsenic have much in common, and the logical grouping is that of the triad, phosphorus-arsenic-antimony, with bismuth standing quite apart. In spite of this apparently well-marked division, one of the difficult problems of microscopic qualitative analysis is that of proving, beyond doubt, the presence of both antimony and bismuth in complex mixtures.

DETECTION OF VANADIUM

In order successfully to separate and identify vanadium, it is essential that its important chemical properties shall be kept in mind.

Vanadium forms four oxides, VO , V_2O_3 , VO_2 and V_2O_5 , giving rise to lavender or violet, green, blue, and yellow compounds, respectively.

From V_2O_3 there is formed $\text{V}_2(\text{SO}_4)_3$ which is able to unite with alkali sulphates to form vanadium alums. In this respect V^{+++} resembles Cr^{+++} and Fe^{+++} ; $\text{VSO}_4 \cdot 7 \text{H}_2\text{O}$ is known, an analogy with Fe^{++} .

V_2O_3 is readily oxidized to V_2O_5 , the analogue of P_2O_5 , whence we have orthovanadates (from H_3VO_4) and metavanadates (from HVO_3). The latter are easily converted into the former when heated in acidified solution.

Unlike phosphorus and arsenic, the trichloride cannot be separated by distilling in a current of chlorine, for VCl_3 is non-volatile and crystallizes in deliquescent plates. But VCl_4 and VCl_5 are distillable, high boiling liquids.

H_2O_2 oxidizes solutions of vanadates to pervanadates, *e.g.*, KVO_4 , a salt analogous to KMnO_4 .

By precipitations we usually obtain the metavanadate, but in fusions with oxidizing agents ortho- (or pyro-) vanadates are formed.

A—Precipitation by Ammonium Chloride — NH_4Cl .

Compound Precipitated — NH_4VO_3 .

To a drop or two of an alkaline solution, believed to contain vanadium, add by Method I a completely saturated solution of NH_4Cl , or add large crystals of NH_4Cl .

Ammonium metavanadate is precipitated in the form of colorless elliptical plates or tiny lenticular, strongly birefringent orthorhombic grains (Fig. 108, page 181). Since this is essentially a method of "salting out" it is important that the test drop shall be concentrated with respect to vanadium. It follows that many other salts may be precipitated with the NH_4VO_3 and may completely mask the reaction.

These colorless crystals of NH_4VO_3 can be converted into a yellow ammonium vanadate of uncertain composition by adding dilute acetic acid and heating the solution. This is accomplished by decanting the supernatant liquid, adding two or three drops of acetic acid, and heating until the metavanadate has dissolved and part of the water evaporated. On standing, as the preparation passes to dryness, yellow four-sided and six-sided plates and tabular crystals separate (Fig. 109, page 181). The four-sided plates have an acute angle of 68° and the six-sided are fourlings with extinction angles of 29° with their elongation; star-like radiating clusters and skeletal forms also separate.

B—By Means of Silver Nitrate — AgNO_3 .

Compound Formed — $\text{Ag}_4\text{V}_2\text{O}_7$.¹

To a moderately concentrated solution of material precipitated by NH_4Cl and thought to be NH_4VO_3 , add a large drop of acetic acid. If the test drop contains vanadium the solution should turn yellow. Place at the edge of the test drop a large fragment of AgNO_3 . Heat the preparation so that both reagent and test drop are hot. While still holding the preparation over the micro-flame, cause the dissolved AgNO_3 to flow into the test drop. Allow the preparation to stand for some time. If vanadium is present, a precipitate of tiny bristling disks or of slender needles or slender prisms, singly, in clumps, and in radiating clusters is obtained (Fig. 110, page 181). These crystals are yellow, orange, dark-red, or brown, or may even be black in appearance. In order to separate the silver vanadate from silver chloride, the silver vana-

¹ Behrens: *Anleitung*, p. 73.

date formed is dissolved in HNO_3 , filtered, and the filtrate is reprecipitated by $\text{NaC}_2\text{H}_3\text{O}_2$.

The character of the first precipitate varies with concentrations and the degree of the acidity with $\text{HC}_2\text{H}_3\text{O}_2$. It may be a dense curdy yellow precipitate or yellow acicular crystals or thin irregular plates. Ag_3AsO_4 behaves in a similar way. (See Silver, page 254.) Ag_3PO_4 forms a yellowish white curdy precipitate changing into three-armed skeletal crystals.

Separations.

1—Fuse the material with KNO_3 , forming potassium vanadate, which is soluble in water. Add $\text{Pb}(\text{NO}_3)_2$ or BaCl_2 , precipitating the V as Pb or Ba vanadate. Decompose the vanadate with H_2SO_4 and neutralize the vanadic acid with NH_4OH . Add a saturated solution of NH_4Cl , thus precipitating NH_4VO_3 .

2—Decompose the material with concentrated HNO_3 . Evaporate the solution. Treat the residue with a concentrated solution of NaOH and Na_2CO_3 . Sodium vanadate is soluble. Add NH_4OH and NH_4Cl , precipitating the meta-vanadate. If Pb is present, it should be removed by H_2S before the treatment with NaOH .

Miscellaneous Reactions.

$\text{K}_4\text{Fe}(\text{CN})_6$: gives a heavy green precipitate insoluble in acids.

Oxalic Acid: reduces to tetravalent V, blue color.

H_2O_2 : reddish-brown solution (Ti = orange or yellow).

Metallic Zn, in HCl or H_2SO_4 reduces to tetravalent V; solution is first green, then blue, then green, and finally lavender blue (divalent V) or violet. Columbates give blue — Tantalates no color. Titanates, blue. Molybdates, blue. (Ru and Rh blue.)

With strychnine sulphate in concentrated H_2SO_4 , bluish-violet coloration changing to rose pink. No color with Cb, Ta, Ti, W.

DETECTION OF COLUMBIUM AND TANTALUM

Unless a considerable quantity of material, relatively high in either columbium or tantalum, is available, the positive identification of these elements is impracticable by micro-methods. Recourse should be had to the spectrograph, or the analyst should

be contented to group the two elements together and report columbium and tantalum present or absent.

Differentiation when dealing with relatively pure materials is always possible, but identification of each element when both are present in complicated mixtures is impracticable.

In micro-analysis columbates or tantalates derived from Cb_2O_5 and Ta_2O_5 are alone encountered. Usually a preliminary test with metallic zinc or metallic tin in HCl or H_2SO_4 solution is advisable. Columbates give a blue to brown color resulting from reduction to CbO_2 and CbO (and even to Cb in part). Tantalates give no color. The blue color is, however, not peculiar to columbium, as we have already seen. (See Ti , V , Mo , W .)

Because of the possible interference of many substances, it is necessary first to accomplish a separation before applying identity tests.

Fuse the material with HKSO_4 ; digest the fused mass in cold water. Most of the columbium and tantalum will be found in the insoluble residue in the form of hydrous pentoxides, more or less contaminated with oxides of Si , Ti , Zr , Fe , Sn , W , etc. Filter and wash. Fuse the residue with NaOH and dissolve in cold water. Sodium columbate and sodium tantalate are insoluble in water containing NaOH . Decant or filter. Add water; the columbate and tantalate are partly dissolved; add dilute H_2SO_4 ; hydrous pentoxides of columbium and tantalum are formed. The freshly precipitated hydrous oxides are readily soluble in HF .

A satisfactory separation of columbium and tantalum can be accomplished by the method of Sears.² The material is fused with several times its volume HNaSO_4 at a bright red heat. The melt is extracted with water, filtered, and the residue is thoroughly washed with hot 3 N HCl to remove the iron, manganese, and other soluble substances. HCl of this concentration dissolves no columbium nor tantalum but more dilute HCl will cause a loss. The white residue containing columbium and tantalum is then treated with H_2SO_4 (1 : 1) and heated until boiling ceases. The precipitate is separated by the centrifuge and the residue washed with cold 6 N H_2SO_4 until the washing liquid gives no precipitate with NH_4OH . Columbium is completely dissolved and tantalum remains in the residue. This procedure is especially applicable to columbite and tantalite.

² *Jour. Amer. Chem. Soc.* **48**, 343 (1926).

To a large drop of a HF solution add KF by Method I. $2 \text{KF} \cdot \text{CbF}_5$ or $2 \text{KF} \cdot \text{CbO} \cdot \text{F}_5 \cdot \text{H}_2\text{O}$ and $2 \text{KF} \cdot \text{TaF}_5$ are formed. Of these two salts the potassium fluotantalate is only sparingly soluble in water, but the potassium fluocolumbate is readily soluble. In mixtures the tantalum salt is the first to separate slowly, forming long thin orthorhombic prisms with square or slightly oblique ends and feeble birefringence (Fig. 111, page 181).

The much more soluble columbium salt appears only after some time has elapsed and spontaneous evaporation has greatly increased the concentration, when tabular crystals and thin plates of the columbium salt may appear.

When the amount of material renders it possible to prepare moderately pure soluble potassium columbate or tantalate, the differentiation of these two elements is often practicable, for upon the addition of a fragment of NaOH the sodium salts are formed; these salts are practically insoluble in water containing NaOH, but are soluble in pure water. The sodium columbate $\text{NaCbO}_3 \cdot 3 \text{H}_2\text{O}$ (Behrens) separates in monoclinic prisms with imperfectly developed ends, exhibiting extinction parallel with the elongation of the prism. Thin six-sided plates are also formed (Figs. 112, 113, page 195). The prisms for the most part form singly, but radiating clusters are also abundant. This monoclinic salt, $\text{NaCbO}_3 \cdot 3 \text{H}_2\text{O}$, is formed only when the NaOH is in but slight excess. If the alkali is added to a neutral or acid solution an acid columbate is precipitated. On the other hand, if the NaOH is added in decided excess, a hexagonal salt separates. It is probable that this salt has the same composition as the sodium tantalate described below.³ In making use of NaOH as reagent for the differentiation of columbium and tantalum it is, therefore, necessary to make several separate tests varying the amount of the NaOH applied to the test drop in order, if possible, to hit upon just the right concentration to obtain a separation of the monoclinic $\text{NaCbO}_3 \cdot 3 \text{H}_2\text{O}$.

Sodium tantalate crystallizes very differently, for the salt formed $\text{Na}_5\text{TaO}_{19} \cdot 25 \text{H}_2\text{O}$ (Haushofer; Behrens) is hexagonal and separates in all the types common to salts of this system that form hexagonal plates, *i.e.*, round drusy disks, skeletons of hexa-

³ W. Behrens: *Tabellen z. Gebrauch b. mikroskop. Arbeiten* (4 Auf., Hirzel, Leipzig, 1908), pp. 193, 200.

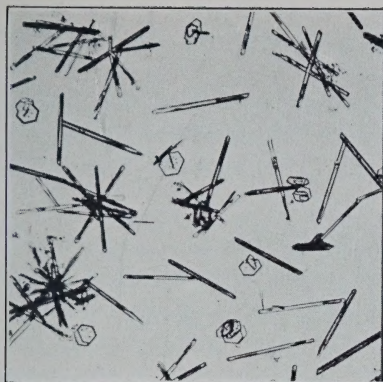


FIG. 112. Columbium Precipitated as Sodium Columbate. 200X.

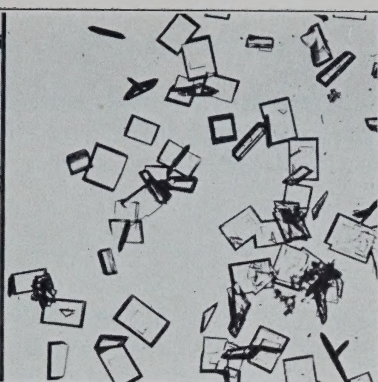


FIG. 113. Sodium Columbate Recrystallized from Hot Water. 100X.

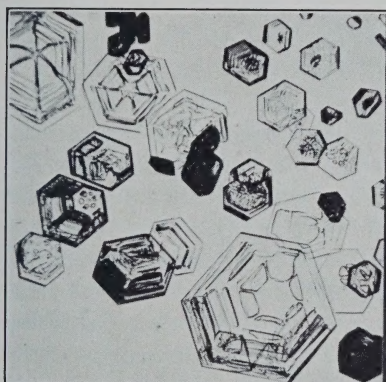


FIG. 114. Antimony with Cesium Chloride. 100X.

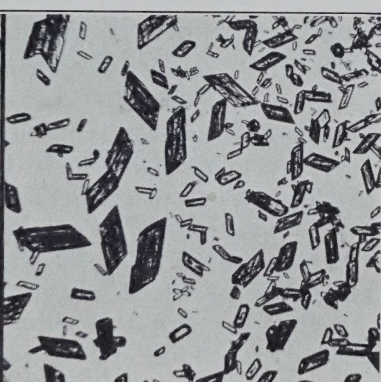


FIG. 115. Antimony with Cesium Chloride in the Presence of too much Nitric Acid. 100X.

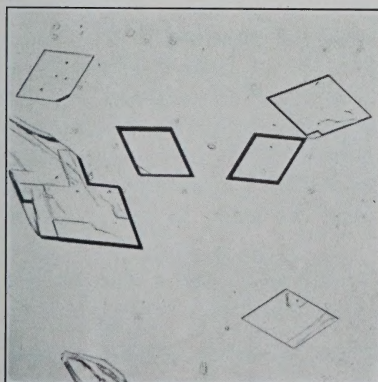


FIG. 116. Bismuth with Cesium Chloride in Excess. 100X.

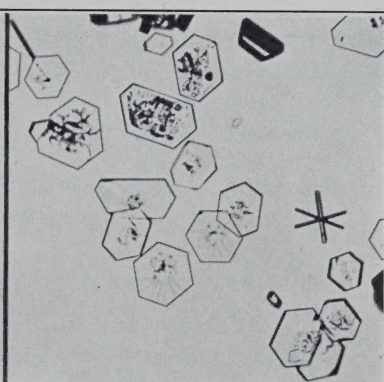


FIG. 117. Bismuth with Cesium Chloride not in Excess. 150X.

gons, rosettes, well-developed hexagons, etc. This salt is probably isomorphous with the sodium columbate of the same composition, and is indistinguishable from it.

DETECTION OF NITROGEN

In inorganic compounds nitrogen is met with as nitrides and as acid oxides of nitrogen united with various positive ions to form salts in which the nitrogen acids are present in various degrees of oxidation. For the detection of these acids see pages 298-310.

For the identification of NH_3 and amines, see page 74.

For N in cyanides, see page 304.

For N in complex cyanides, see page 307.

For N in thiocyanates, see page 306.

Nitrogen in organic compounds may be identified as follows. Into a tube of hard glass similar to that shown in Fig. 27, page 44, introduce a small amount of the finely powdered substance. Push down into the tube by means of an iron wire several tiny shavings of metallic sodium. The shavings should be in close contact with the powdered material. Heat the sodium very carefully so that in melting it comes in intimate contact with the material, then raise the temperature gradually until it is judged from appearances that a reaction has taken place and NaCN has been formed. Cool, cut off the portion of the tube containing the fused mass, crush and extract with warm water; add to the solution a little FeSO_4 , heat almost to boiling, and filter, decant or centrifuge. To the clear solution add HCl until distinctly acid. A dark-blue precipitate of Prussian blue indicates the presence of N in the compound tested.⁴

DETECTION OF PHOSPHORUS

Preliminary Treatment. — If the material is soluble in water, add HNO_3 , heat the preparation and set aside to cool. When cold, test as below.

If the material is insoluble fuse with Na_2CO_3 and a little KNO_3 so as to obtain a soluble phosphate. Dissolve in water, acidify

⁴ Emich: *Lehrbuch der Mikrochemie*, p. 197. (Bergmann, München 1926.)

with HNO_3 , and evaporate to dryness, keeping the temperature below the boiling point. This material is dissolved in dilute HNO_3 and tested for PO_4^{---}

A—By Means of Ammonium Molybdate — $(\text{NH}_4)_5\text{H}_7(\text{MoO}_4)_6$.

Compound Formed — $(\text{NH}_4)_3\text{PO}_4 \cdot 10 \text{ MoO}_3 \cdot \text{H}_2\text{O}$.

To the dilute test drop add HNO_3 until it is strongly acid. Prepare a drop or two of a moderately concentrated solution of the reagent; add thereto a drop of HNO_3 (1 : 4) and warm the reagent mixture; no precipitate should form. If the reagent mixture remains clear, apply a drop when cold, to the test drop by Method I. If a precipitate is formed in the reagent, add more HNO_3 until the precipitate redissolves.

Ammonium phosphomolybdate separates slowly in the cold as a fine, granular, isotropic, yellow precipitate; later spherical grains appear and finally cubes and rounded octahedra. Warming the preparation hastens the reaction, but may cause the separation of other complex molybdates (Fig. 124, page 223).

This reaction, though sensitive, is not specific for phosphorus, for analogous molybdenum compounds are formed with silicon, vanadium and arsenic, which are not distinguishable from the phosphomolybdate.

Behrens has suggested that the test be made in the cold, for the phosphomolybdate may then be known because of its more rapid separation than is the case of the other complex molybdates. This requires a definite knowledge of concentrations in the test drop and the development of a high degree of discriminatory observation.

In spite of the fact that this reaction is not specific it is the one that should be tried first, for it is sensitive, is subject to practically no interferences, and requires no care in the adjustment of conditions, other than the avoiding of too much HNO_3 . Too much HNO_3 may cause a precipitation of molybdic acid, but since this is white it cannot be mistaken for the yellow ammonium phosphomolybdate.

See Silicon, page 174.

Experiment.

(a) — Test a phosphate and an arsenate with ammonium molybdate.

B—By Means of Magnesium Acetate in Ammoniacal Solution.*Compound Formed* — $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.

Add to the test drop several large fragments of NH_4Cl and when these are dissolved, the drop is made *strongly* ammoniacal with NH_4OH ; finally a moderately concentrated solution of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ is added by Method I.

Orthophosphates yield a precipitate at once as a heavy granular mass. This apparently amorphous material is rapidly converted into large six-pointed dendritic stars and irregular feathery fragments (Fig. 74, page 113). These skeletal crystals soon develop into characteristic orthorhombic prisms shaped like the roofs of houses, or they take a form resembling envelopes; if these are not fully filled out they appear as H's or X's (Fig. 75, page 113).

The feathery stars, changing into prisms, are the most characteristic forms assumed by the reaction product. When non-characteristic crystals are obtained and doubt arises as to their nature, decant, dissolve the crystals in dilute HCl and allow a drop of strong NH_4OH to flow into the HCl solution. $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ will be again precipitated and will probably now appear in crystals easily identified.

Arsenates form $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$, indistinguishable from the analogous phosphate and isomorphous with it. Ammonium magnesium phosphate separates from solutions that are weakly ammoniacal, but the corresponding arsenate requires a solution very strongly ammoniacal in order that the crystals can be made to appear. The difference is sometimes sufficiently marked to afford a clue as to which compound is present, or whether both are present.

To determine whether a crystalline precipitate is phosphate or arsenate, proceed as follows. Decant the mother liquor and wash the crystals thoroughly with water containing a little NH_4OH . This is usually readily accomplished since the crystals cling tenaciously to the glass and permit washing without becoming loosened from the object slide. Dissolve the insoluble residue in acetic acid (1 : 4). Add AgNO_3 by Method I. Silver phosphate separates at once as a lemon-yellow dense curdy or granular precipitate. In a few minutes irregular crystallites appear, but the crystals obtained are rarely sufficiently well developed to offer a means of identification other than the color (Fig. 158, page 311); but here too there is uncertainty, for silver arsenite is also yellow. Silver arsenate is reddish-brown, or chestnut brown or even a

brownish lavender. It crystallizes in a great variety of forms (see Silver, page 254), is readily soluble in NH_4OH and in HNO_3 , from which it may be recrystallized in more characteristic forms than those in which it was originally precipitated (Figs. 156, 157, page 311).

For further data see Detection of Anions, pages 318–320.

Experiments.

(a) — Test a phosphate and an arsenate with magnesium acetate and NH_4OH .

(b) — Recrystallize the ammonium magnesium phosphate precipitate by dissolving in HCl and adding NH_4OH .

DETECTION OF ARSENIC

Arsenic is ordinarily met with in four combinations: as the oxide As_2O_3 ; as alkali arsenites corresponding to the formula $M\text{AsO}_2$, and complex arsenites of the heavy metals, of uncertain composition; as arsenates derived from orthoarsenic acid H_3AsO_4 ; or as "metallic" arsenic and arsenides in alloys.

The attempt to identify the compound of arsenic should follow the detection of the element, the latter is most easily done by converting it into AsH_3 and applying suitable tests for this gas.

In some combinations it may be necessary to separate the arsenic by heating in a hard glass tube in a current of chlorine. AsCl_3 and AsCl_5 can be thus expelled, absorbed, and tested for. Boiling materials with concentrated HCl may lead to a loss of arsenic as chlorides unless some element such as sodium or potassium is present to hold the arsenic as an arsenate; but even under these conditions there may be a loss.

It is well to bear in mind that arsenites are not readily oxidized to arsenates. The addition of HNO_3 to some of them will cause a precipitation of crystalline As_2O_3 . As_2O_3 can be recrystallized from moderately strong HNO_3 .

A-Detection as Arsine — AsH_3 .

Compound Formed — $\text{AgNO}_3 \cdot \text{Ag}_3\text{As}$.

For the generation of AsH_3 on a "micro" scale the retort-like tube illustrated in Figs. 8, 23, pages 17, 42, has been found convenient. The final set-up is shown in Fig. 24, page 42.

Fit the side tube with a tightly fitting plug of *soft* wood *P*, Fig. 23. Introduce into the tube several bright fragments of

arsenic-free zinc, *Z*. By means of a suitable pipette introduce dilute, arsenic-free, HCl. The acid will occupy the space *A* as shown in Fig. 23. It will not flow down upon the zinc as long as the wooden plug *P* is tightly in place. A plug of absorbent cotton, which has previously been soaked in lead acetate and dried, is loosely inserted as shown at *C*. The capillary tube *T* containing a tiny crystal of AgNO_3 , *S*, and a somewhat larger fragment of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, *L*, is attached to the generator by the tightly fitting ring of rubber tubing *R*. The wooden plug *P* is removed for a moment and the acid allowed to flow down upon the zinc. A drop of water *s* is introduced into the side tube and the wooden plug reinserted. The water swells the wood and makes a gas-tight seal.

The apparatus is now in the position shown in Fig. 23, with *T* so held upon the stage of the microscope by means of the stage clips that the crystals *L* and *S* are in the field of a low-power objective. From time to time these crystals are examined to see if they change color. If, after a short time, *S* remains unchanged, clear and colorless, the reagents are free from arsenic.

Carefully remove the wooden plug and, by means of a capillary tube, introduce several drops of a HCl solution of the material to be tested. Plug securely and watch the fragment of AgNO_3 at *S*.

If arsenic is present, AsH_3 is formed and the AgNO_3 crystal turns first a lemon yellow due to the formation of a compound believed to have the composition $\text{AgNO}_3 \cdot \text{Ag}_3\text{As}$. The yellow color is fugitive and the crystal eventually turns black by reason of reduction to metallic silver. The lead acetate crystal remains unchanged unless H_2S is evolved. The lead-acetate cotton *C* should hold back all H_2S formed unless in excessive amount. The crystal serves, therefore, as an indicator that no H_2S has passed over into the capillary tube *T*. This indication is essential since H_2S will turn AgNO_3 crystals black because of the formation of black Ag_2S .

With antimony, SbH_3 is obtained, which acts upon the AgNO_3 in a manner similar to AsH_3 , but a yellow compound is practically never seen, the crystal becoming black at once. A yellow color persisting for a few seconds can therefore generally be considered as proof that arsenic is present.

Phosphine turns the AgNO_3 black at once; there is no transi-

tional yellow-colored compound formed. The $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ is unaffected and does not hold back PH_3 . If it is suspected that phosphine may be formed in the generator it can be held back by placing below *C* a plug of absorbent cotton saturated with a HCl solution of cuprous chloride. When the crystal of AgNO_3 turns black at once SbH_3 or PH_3 has been formed or the evolution of AsH_3 has been so rapid that the formation of the yellow compound may have been overlooked. In such an event AsH_3 should be sought by evolution through the action of metallic aluminum and KOH .

If only a very little antimony is present and much arsenic, a few bits of bright platinum wire may be introduced in contact with the zinc. Antimony is deposited upon the platinum as a velvety black coating.

To differentiate further between antimony and arsenic the hydrides may be generated through the action of KOH on metallic aluminum; under these conditions AsH_3 is alone evolved, and the antimony is deposited upon the aluminum and in part precipitated.

In place of the AgNO_3 at *S* a fragment of HgBr_2 may be used, or a textile fiber soaked in HgBr_2 and subsequently dried, or HgBr_2 -paper can be employed. If a fiber is used the internal diameter of the tube *T* must be such that the fiber practically fills it. Arsine turns mercuric bromide red or brown; stibine behaves similarly.

The detection of very minute amounts of arsenic as AsH_3 in the presence of iron is usually impossible, since the iron prevents the evolution of AsH_3 .

B—By Reduction to Metallic Arsenic and Subsequent Oxidation to Arsenic Trioxide — As_2O_3 .

The well-dried, finely powdered material is mixed with several times its volume of *anhydrous* potassium ferrocyanide. A portion of the mixture is placed in a subliming tube (Fig. 27, page 44), and well tapped down so that all the mixture collects at the sealed tip of the tube.

Heat the mixture gently at first, gradually raising the temperature until it reaches a dull red and the glass begins to soften. The arsenical compound is reduced and "metallic" arsenic is deposited upon the walls of the tube as a blackish or brownish

mirror; the latter type of mirror is the result of a partial oxidation of the arsenic.

Antimony yields a blacker or silvery mirror. Mercury gives tiny silvery spheres.

Certain compounds of carbon and compounds of sulphur may, under certain conditions, yield a deposit on the walls of the tube so closely resembling the brown "mirror" of arsenic as not to be distinguished therefrom by color alone.

To guard against misinterpretation, the sealed end of the tube is cut off and the mirror heated carefully, holding the tube inclined so as to induce a current of air to flow through the tube. Arsenic will be oxidized and will be sublimed as As_2O_3 in the form of brilliant highly refractive ($n = 1.755$) isotropic octahedra. The crystals are soluble in KOH, forming KAsO_2 , and are reprecipitated by HNO_3 as well-developed octahedra. The potassium arsenite can be further tested as described below.

Arsenical compounds can be reduced to "metallic" arsenic by heating to boiling in HCl solution with a fragment of bright copper foil or copper wire. Arsenic colors the copper a smoky gray. Wash the coated copper with water and alcohol, dry very thoroughly and drop into a subliming tube. On heating, As_2O_3 is formed, which can be identified as described above or converted into AsH_3 and tested as above. (See also Mercury, page 142.)

C-Distinction between Arsenites and Arsenates.

1-Strong HNO_3 usually precipitates As_2O_3 in glistening isotropic octahedra from concentrated solutions of arsenites, but no such precipitation takes place in concentrated solutions of arsenates.

2-A solution of silver nitrate (or better ammoniacal silver nitrate) reacts with an ammoniacal solution of arsenites, yielding lemon-yellow Ag_3AsO_3 (?) as a curdy or granular precipitate which soon changes into minute acicular crystals; these crystals in turn grow into thin rods with notched ends or into long slender acicular prisms. On long standing oxidation is likely to take place, giving rise to crystals of silver arsenate. Silver arsenate is soluble in acids and also in strong NH_4OH ; hence the test may fail if the preparation is not examined at once, or if the drop and the reagent are too strongly ammoniacal.

Silver arsenate is precipitated in red, reddish-brown or garnet-

colored plates, dendrites and skeleton crystals, the appearance and properties of which are discussed on page 254.

Silver arsenite cannot be confused with silver arsenate and there is little danger of a failure of the test. But silver arsenate resembles silver chromate and silver bichromate in color, and if in tiny crystals may be confused with these salts. The silver nitrate test for AsO_4^{---} cannot be considered as conclusive unless CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ have been proved to be absent. In the recrystallization of Ag_3AsO_4 in HNO_3 , colorless octahedral crystals of As_2O_3 may separate if Ag_3AsO_3 is also present.

3—A strongly ammoniacal solution of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ containing sufficient NH_4Cl to keep the magnesium in solution, when added to a solution of arsenates, gives a precipitate of $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, isomorphous with $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. The color, habit, and behavior, of the two compounds toward acids are identical. The descriptions given for the double phosphate on pages 77, and 121–123 apply equally well to the double arsenate.

Arsenites give a flocculent or granular precipitate but no crystals of the type obtainable with arsenates.

DETECTION OF ANTIMONY AND BISMUTH

Antimony and bismuth are so closely related that their differentiation by microscopical tests is difficult and usually unsatisfactory when both are present in the material to be analysed, but singly their identification is simple and rapid.

Tin is first removed by treatment with HNO_3 . Much, sometimes all, the antimony separates with the SnO_2 as Sb_2O_4 . (See Tin, page 178.) Repeated extractions with HNO_3 (1.20 sp. gr.) will not always remove the Sb_2O_4 . It is usually best to redissolve the SnO_2 and reprecipitate by evaporating with HNO_3 . All HNO_3 solutions and extracts are united and concentrated to small bulk or until the excess of free HNO_3 is driven off. Add a tiny drop of water and view the preparation over a black background. A white turbidity, white precipitate, or white cloud indicates that antimony or bismuth, or both, are probably present. Stir the preparation so as to complete the hydrolysis, then add HCl cautiously until the basic nitrates are completely redissolved, but care must be used to avoid any more HCl than just sufficient to bring the antimonyl or bismuthyl salt into solution. Concen-

trate if necessary and *test as below*. When evaporating a low temperature should be employed, for antimony chloride is volatile.

A—By Means of Cesium Chloride — CsCl.

Compounds Formed — $3 \text{ CsCl} \cdot 2 \text{ SbCl}_3$ (Hexagonal)⁵

$3 \text{ CsCl} \cdot 2 \text{ BiCl}_3$ (Hexagonal)

$3 \text{ CsCl} \cdot \text{BiCl}_3$ (Rhombic).

To the moderately concentrated solution acidified with HCl add a large fragment of CsCl. (Method II, page 32.)

Antimony gives at once, thin, colorless disks, with irregular edges, irregular six-pointed stars, rosettes, well-formed hexagonal plates, and elongated hexagonal plates. The hexagons usually show a system of straight or curving ribs extending from the center to the angles of the hexagons. (Fig. 114, page 195.)

If the CsCl has been properly applied in considerable excess, bismuth yields thin colorless rhombs, singly and in aggregates (Fig. 116, page 195), but if the reagent is not in excess, hexagonal plates, stars or disks are obtained, not to be distinguished from those formed by antimony (Fig. 117, page 195).

Bismuth salts are thus readily differentiated from those of antimony, but in mixtures of antimony and bismuth hexagonal plates alone are obtained.

Conversion into orange or red iodo-compounds by introducing a fragment of KI into the test drop increases the sensitivity of the reaction. This reaction is slow and time must be given for the development of the orange-yellow or orange-red compounds. The cesium iodo-bismuthate is darker in color than the iodo-antimonate and of a different shade, but this difference is not sufficiently marked to be dependable as a means of differentiation, for crystals of greatly varying thickness are always obtained, and therefore

⁵ Various formulas have been given for the reaction products. Behrens (*Anleitung*, p. 108) states that the double salts are $2 \text{ CsCl} \cdot \text{SbCl}_3 \cdot 2\frac{1}{2} \text{ H}_2\text{O}$ and $2 \text{ CsCl} \cdot \text{BiCl}_3 \cdot 2\frac{1}{2} \text{ H}_2\text{O}$. Vermande: *Pharm. Weekblad* **55**, 1131 (1918) gives the formulas above; the rhombic crystals of $3 \text{ CsCl} \cdot \text{BiCl}_3$ are only formed if a large excess of CsCl is present. Ducloux: *Mikrochemie* **2**, 108 (1924) gives a number of other formulas for different double cesium chlorides of antimony and bismuth, but apparently he has studied only the 3 : 2 salt. The work of Meloche and Clark: *Jour. Amer. Chem. Soc.* **52**, 907 (1930) on $3 \text{ CsI} \cdot 2 \text{ BiI}_3$, which is hexagonal, confirms the analogous formula for the isomorphous $3 \text{ CsCl} \cdot 2 \text{ BiCl}_3$.

the color intensities and hues of the hexagonal plates differ greatly according to their thickness.

In analytical practice, it is unwise to add the KI until the chloro-compounds have separated in sufficient amount to show the hexagons of the antimony salt or the rhombs of the bismuth salt, for the iodo-salts of both antimony and bismuth form hexagons but no rhombs. If the rhombs of cesium chloro-bismuthate have already been formed before the introduction of the iodide, they will be gradually colored since the iodo-salt forms a pseudomorph after the chloro-salt; small deep-colored hexagons will eventually appear.

The compositions of the iodo-compounds are even better established than those of the chloro-compounds; the weight of evidence appears to indicate that three molecules of CsI unite with two molecules of SbI_3 or BiI_3 rather than SbI_4 or BiI_4 . Iodine is almost always set free in performing this test, appearing as irregular skeletal fragments and prisms. Not infrequently well-developed rhombs are formed. These rhombs are practically opaque and are therefore black by transmitted light. Inexperienced analysts may mistake such crystals of iodine for very dark-colored crystals of the double iodo-salt of antimony or of bismuth.

It is essential that the KI be added to the test drop at room temperature, since if warm, BiI_3 may be thrown down as a dense granular brown or black precipitate.

Polarized light affords a means of more easily differentiating between the rhombs of bismuth and the hexagons of antimony, for the rhombs are orthorhombic and strongly birefringent, while the antimony salt is hexagonal and usually so orientated as to be isotropic. Therefore any rhombs in the midst of hexagons can be readily found. Since bismuth forms both rhombs and hexagons examination between crossed nicols should never be omitted.

Tin (See page 177) with CsCl gives very insoluble cubes or octahedra (as will silver), and if present will take up the CsCl first; hence the antimony or bismuth salt will not be formed until all the tin has been precipitated. In order to avoid this complication the tin should be removed with HNO_3 before testing for antimony and bismuth. The excess of HNO_3 must be fumed off, otherwise typical crystals cannot be obtained (Fig. 115, page 195).

The substitution of a mixture of RbCl and CsCl for pure CsCl in testing for antimony and bismuth often assures a better formation of rhombs of the bismuth salt.

CsCl readily unites with the chlorides of many elements to form easily crystallizable double salts of solubilities such that they may separate under the conditions which obtain in this test.

Given the proper concentrations we may expect that the addition of solid CsCl may be followed by the separation of double cesium chlorides or insoluble simple chlorides of the following elements: Sb, Bi, Cu, Ag, Mg, Zn, Cd, Hg, Sn, Pb, Mn, Ni, Co, Fe, In, Ru, Rh, Pd, Pt. Some of these salts are, strictly speaking, not double chlorides, but cesium salts of complex ions. The most important of these chlorides have already been discussed on pages 140, 141.

Cadmium forms $\text{CsCl} \cdot \text{CdCl}_2$, bipyramidal twins of low solubility, which when first precipitated may be mistaken for octahedra of Cs_2SnCl_6 . There can be no danger of confusion, however, if the preparation is examined with polarized light, for the cadmium salt is anisotropic whereas the tin salt is isotropic.

Under the conditions imposed in the test as indicated above no cesium double chlorides will separate with the alkalis, nor with Ca, Sr, Ba, Al, Cr, nor As (Vermande).

Many of the cesium double salts will be converted into iodo-compounds when KI is added, but in the majority of cases iodine is set free to such an extent as to mask the crystals which may separate.

Experiments.

- (a) — Try the test on an Sb salt.
- (b) — Test a Bi salt using Method I, page 30. Repeat using Method II, page 32.
- (c) — Try converting the chloro-salts of these two elements to the iodo-compounds.
- (d) — Test mixtures of Sb, Bi, Cu, and Sn.

B-By Means of Potassium or Cesium Sulphate — K_2SO_4 or Cs_2SO_4 .

Compound Formed — $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$, or $3 \text{Cs}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$.

The material to be tested is converted into sulphate and to this test drop a fragment of K_2SO_4 or Cs_2SO_4 is added. The details of this test, precautions to be observed, and sources of error have been discussed at length under Sodium, page 58, and Potassium, page 60.

The double salt $3 \text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3$ crystallizes in thin colorless

disks having irregular outlines, in six-pointed stars and rosettes and in symmetrical well-formed hexagons (Fig. 118, page 209).

Antimony forms no compound similar in appearance, hence this test affords a means of differentiating between bismuth and antimony.

C—By Means of Potassium Bioxalate — $\text{HK}(\text{C}_2\text{O}_4)$.

Compounds Formed — $\text{KBi}(\text{C}_2\text{O}_4)_2 \cdot 7\frac{1}{2} \text{H}_2\text{O} (?)$

$\text{SbOH} \cdot \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}.$ ⁶

To the test drop, which should contain no more than just sufficient HNO_3 to keep the antimony or bismuth in solution, add a moderately large fragment of $\text{HK}(\text{C}_2\text{O}_4)$.

With salts of antimony there is obtained a basic oxalate in the form of trichites; but with bismuth acicular crystals and rhombs are obtained. If the preparation is warmed, the bismuth salt separates in tiny tetragonal octahedra. (See Alkaline Earths, page 110, (Fig. 67, page 109.)) Although the oxalate reaction is an excellent method for differentiating between antimony and bismuth in the case of simple salts of these metals, the test is valueless in mixtures since a number of other elements give crystals with $\text{HK}(\text{C}_2\text{O}_4)$ so closely resembling those of antimony and bismuth as to be indistinguishable from them.

D—By Evolution as Stibine — SbH_3 . — In the presence of nascent hydrogen SbH_3 is formed, and may be identified by passing the gas over a fragment of AgNO_3 . AsH_3 first turns the AgNO_3 yellow, then black, but SbH_3 turns the crystal black at once.

If the hydrogen is produced by the action of HCl and metallic zinc both arsine and stibine are formed, but when metallic aluminum and KOH are used to generate the hydrogen only AsH_3 is evolved. (See Arsenic, page 199.)

Bismuth forms no volatile hydride under the conditions of the test and antimony may therefore be detected in the presence of bismuth.

A convenient form of apparatus for the performance of this test is shown in Fig. 24, page 42 and has already been described under Arsenic.

⁶ Behrens: *Anleitung z. Mikrochem. Anal.*, p. 108.

Differentiation between the blackening of the AgNO_3 crystal by SbH_3 and that brought about by PH_3 can be accomplished by repeating the test with metallic zinc and HCl , but before the evolution starts a strip of platinum foil is introduced into the generator and placed in close contact with the pieces of zinc. Under these conditions, metallic antimony is deposited as a velvety black coating upon the platinum and no SbH_4 is evolved, but the evolution of PH_3 (or AsH_3) is unaffected. The black coating of antimony can be dissolved and subjected to confirmatory tests.

E-Differentiation between Antimony and Bismuth by Conversion into Antimonyl Tartrate.

Compounds Formed — Potassium Antimonyl Tartrate, $\text{KSbO} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$; or Barium Antimonyl Tartrate⁷, $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$.

The material to be tested is brought into solution as a chloride; concentrated at as low a heat as is practicable to drive off the excess of HCl but avoiding volatilizing any SbCl_3 . Water or oxalic acid is added to precipitate SbOCl or $(\text{SbO})_2\text{C}_2\text{O}_4$. Decant, filter, or centrifuge. Dissolve the residue in tartaric acid, in which the corresponding bismuthyl salts are practically insoluble. Filter or centrifuge if necessary.

Concentrate the clear tartrate solution and divide it into two parts. To one portion add KCl by Method I, page 30, and allow the preparation to stand and undergo spontaneous evaporation. Examine at frequent intervals. $\text{KSbO} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ separates in colorless highly refractive ($\beta = 1.636$) tetrahedra, square, rectangular, and six-sided plates and tablets of the orthorhombic system. If no distinct crystals appear but a crust forms around the test drop, crush some of the crust and draw it across the drop, thus "seeding" the preparation (Fig. 119, page 209).

The second portion is diluted, acidulated with acetic acid, heated, and into the hot test drop a hot drop of a solution of BaCl_2 or $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ is caused to flow. $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot x\text{H}_2\text{O}$ is formed and separates in thin glistening symmetrical and elongated

⁷ The formula of the barium salt is still in doubt. Groth gives $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot \text{H}_2\text{O}$, tetragonal (+) and $\text{Ba}(\text{SbO})_2 \cdot (\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$, orthorhombic (-). H. Behrens describes the salt as a dihydrated compound and W. Behrens also considers it as dihydrated, orthorhombic with weak negative birefringence.

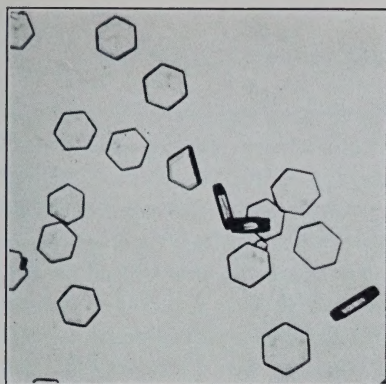


FIG. 118. Bismuth with Cesium Sulphate. 100 $\times$.

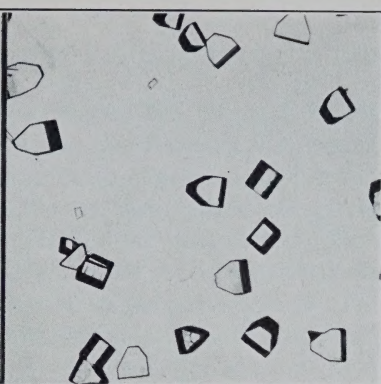


FIG. 119. Antimony Precipitated as Potassium Antimonyl Tartrate. 100 $\times$.

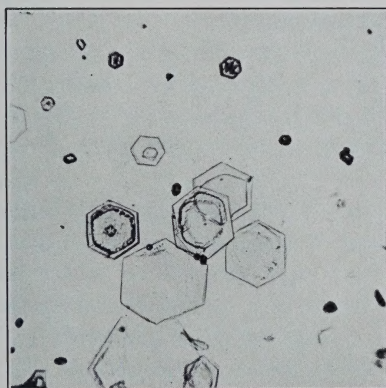


FIG. 120. Molybdenum (MoO_4^{++}) with Thallous Nitrate. 100 $\times$.



FIG. 121. Tungsten (WO_4^{++}) with Thallous Nitrate. 100 $\times$.



FIG. 122. Chromium (CrO_4^{++}) with Thallous Nitrate. 100 $\times$.

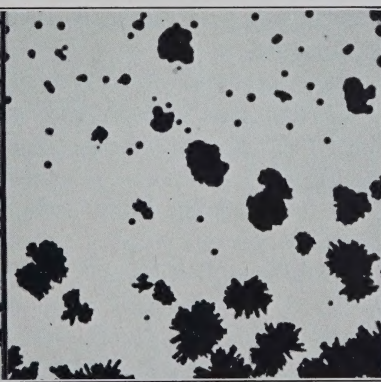


FIG. 123. Manganese (Mn^{++}) with Potassium Chromate. 100 $\times$.

six-sided plates and tablets of the orthorhombic system. There is always a marked tendency to form imbricated aggregates.

The reaction of potassium antimonyl tartrate with silver nitrate giving rise to the formation of large characteristic crystals of silver antimonyl tartrate⁸ is impracticable when dealing with mixtures since the material to be tested almost invariably contains chlorides.

In the case of simple salts either of these double tartrates of antimonyl are excellent and reliable for the identification of antimony and its differentiation from bismuth, but unfortunately the tests fail when dealing with mixtures containing cations other than $(\text{SbO})^+$ or $(\text{BiO})^+$.

Double tartrates corresponding to the general formula $M^+\text{SbO}(\text{C}_4\text{H}_4\text{O}_6)\cdot\text{H}_2\text{O}$ are known where M^+ may be Na^+ , K^+ , Rb^+ , Cs^+ , $(\text{NH}_4)^+$, Ag^+ , or Tl^+ ; all are orthorhombic.

With bivalent elements the salts are $M^{++}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2$ or $M^{++}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2\cdot n\text{H}_2\text{O}$. Of the crystalline anhydrous double tartrates described are those of Sr^{++} (Hex.) and Pb^{++} (Hex.); and of the hydrated salts are Ca^{++} (Ortho.); Ca^{++} (Tetrag.?); Ba^{++} (Tetrag.); Pb^{++} (Mono.).

The double tartrates of antimonyl with monovalent and with bivalent cations form a long series of crystalline *mixed* double salts.

It is therefore obvious that the occurrence of any of these possible combinations can seriously interfere with the interpretation of a test for antimony, and should make clear the necessity of separating antimony from other elements before attempting to apply the tartrate test.

F—Identification of Antimony by Conversion into Sodium Pyroantimonate.

Compound Formed — $\text{H}_2\text{Na}_2\text{Sb}_2\text{O}_7\cdot 6\text{H}_2\text{O}$.

In order that a satisfactory test can be obtained the antimony must be as free as possible from other elements and must be converted into a compound in which pentavalent antimony is present. To accomplish the latter several methods are possible, of which two only need be given.

1—*Fusion with KNO_3 (H. Behrens).* — The antimony compound obtained by separation methods is fused with *several times* its weight of KNO_3 . The mixture is fused and maintained at a red

⁸ Kofler: *Arch. f. Pharm.* **256**, 249 (1918).

heat until most of the nitrate has been driven off. There is always likely to be a considerable loss of antimony during this process. The fused mass is thoroughly cooled and is extracted repeatedly with small amounts of *cold* water. The residue of potassium pyroantimonate is dissolved in boiling water and filtered while hot from any insoluble residue. To a drop of the clear concentrated solution, a drop of a concentrated solution of NaCl is added by Method I, page 30. Sodium pyroantimonate separates almost at once in the form of tiny fusiform and lenticular grains which soon attain a considerable size and tend to unite into more or less bristling globular masses (Fig. 37, page 61).

If the precipitation is made in dilute solutions tetragonal tablets, tetrahedra, and "octahedra" are obtained, but these crystals though better developed are by no means as characteristic of antimony and of sodium as are the fusiform grains.

Lithium and magnesium give with potassium pyroantimonate hexagonal plates and tablets (Fig. 38, page 61). The alkaline earths yield "amorphous" precipitates as do most bivalent elements.

2-To avoid the possible losses resulting from fusion at a high temperature, Schoorl has proposed conversion into pentavalent antimony by boiling with aqua regia. The solution of SbCl_5 thus obtained is carefully concentrated, keeping the temperature below that which would cause a decomposition of SbCl_5 to SbCl_3 (which is volatile). This concentration to dryness is essential and introduces a danger of loss of antimony almost as great as that involved in the fusion method.

To the dry residue a little water is added and sufficient KOH to make the drop strongly alkaline. The mixture is brought to a boil and the concentrated solution of potassium pyroantimonate is decanted from any insoluble residue and to the clear solution NaCl is added as described above. Fusiform and lenticular crystals of $\text{H}_2\text{Na}_2\text{Sb}_2\text{O}_7 \cdot 6 \text{H}_2\text{O}$ are obtained if antimony is present (Fig. 37, page 61).

Neither arsenic nor bismuth interferes unless present in large amount.

CHAPTER VIII

DETECTION OF THE ELEMENTS OF GROUP VI

O; Cr; Mo, W; U; S, Se, Te

The transition element of Group VI is oxygen; the primary sub-group consists of chromium, molybdenum, tungsten, and uranium, and the secondary sub-group of sulphur, selenium, and tellurium.

Considered merely from the point of view of microscopic analysis, Group VI may be divided into the following groups: O; Cr; Mo, W; U; S, Se, Te.

Considered in relation to their positions in the Periodic System, the elements in Group VI offer many highly interesting analogies. Many oxides are isomorphous with the corresponding sulphides. Most of the orthorhombic alkali sulphates are isomorphous with their corresponding selenates, chromates, molybdates, and tungstates; a similar relation holds for the orthorhombic BaSO_4 , BaSeO_4 , and BaCrO_4 . Silver sulphate is isomorphous with silver chromate and silver selenate. Similar isomorphous series are to be met with in many double salts, as for example in $\text{K}_2\text{Mg}(\text{SO}_4, \text{SeO}_4, \text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Na}_3\text{Li}(\text{SO}_4, \text{SeO}_4, \text{CrO}_4, \text{MoO}_4, \text{WO}_4)_2 \cdot 6\text{H}_2\text{O}$; in the "vitriols"; and in the "alums." Chromium shows horizontal analogies, for it forms "alums" isomorphous with those of manganese, iron, and vanadium (and all other "alums").

Although the instances of isomorphism are very numerous and striking in compounds of chromium, molybdenum, and tungsten and in those of sulphur and selenium, and between the first sub-group and sulphur and selenium, there are few cases of definitely established isomorphism of compounds of uranium or of tellurium with the other members of Group VI. Uranium is therefore easily detected and tellurium likewise, providing selenium is not also present.

For the transitional element oxygen we have at present no known direct microscopical qualitative test. It may of course be made to combine with hydrogen to form H_2O and the H_2O formed iden-

tified, but this requires a more or less complicated combustion apparatus and is impracticable for occasional tests only. Methods based upon liberating oxygen and its absorption by suitable reagents are also impracticable. Microscopic tests are also lacking for ozone and for hydrogen peroxide. Such tests as may be employed, as for example KI and starch, benzidine, etc., are based upon recognition of oxidizing power, but none of them are specific for any one compound.

The identification of oxides and of basic salts must therefore be based upon their physical appearance and properties and upon their general chemical behavior. The presumption of the presence of oxides must rest largely upon negative evidence; that is, the analyst must reach a decision by elimination. This necessitates clear thinking founded upon a rather comprehensive knowledge of the chemical properties of the elements (or ions) found to be present and an ability to visualize the reactions that the combination in hand might be expected to exhibit under the conditions to which it is being subjected by the analyst. It is not possible to formulate any directions for a general plan of attack.

DETECTION OF CHROMIUM

Chromium forms both chromous and chromic salts and chromates. The oxide Cr_2O_3 acts as a weak base and does not form salts with weak acids. The oxide CrO_3 comports itself as a strong acid.

Chromous salts are very unstable and easily oxidized, resembling ferrous salts, but are even less stable than the latter. They therefore rarely, if ever, occur in routine qualitative analysis.

All chromic salts are colored and occur in two modifications, one green, the other violet. It is now generally accepted that the green solutions contain complex ions and that we do not have simple Cr^{+++} ions present.⁹ Such solutions may not give specific reactions for chromium, nor for the mineral acid present. The violet-colored salts behave normally. Both modifications are generally present in solutions.

Certain anhydrous violet-colored compounds, *e.g.*, CrCl_3 ,

⁹ See Weiser: *The Hydrous Oxides* (McGraw-Hill, New York, 1926), p. 71.

Urbain et S  n  chal: *Introduction    la chimie des complexes* (Hermann, Paris, 1913).

CrBr_3 , $\text{Cr}_2(\text{SO}_4)_3$, are insoluble in both cold and hot water and also in dilute and in concentrated acids, but are readily soluble in water in the presence of SnCl_2 (or if they contain traces of chromous salts).

The oxide CrO_3 forms the chromate ion CrO_4^{--} , the dichromate ion $\text{Cr}_2\text{O}_7^{--}$, the trichromate ion $\text{Cr}_3\text{O}_{10}^{--}$, and several polychromate ions of somewhat uncertain composition. The salts of CrO_4^{--} are yellow; those of $\text{Cr}_2\text{O}_7^{--}$ and more complex ions are red. No acid chromates are known.

Chromium forms no "basic acetate"; in this it resembles manganese and differs from iron and aluminum.

The addition of KOH or NaOH to solutions of chromic salts precipitates a grayish green or grayish violet hydrous oxide which *when freshly precipitated* is soluble in excess of the reagent (forming an alkali chromite) but is completely reprecipitated on boiling (thus differing from aluminum). The solubility in excess of the alkali in the cold may be very incomplete in the presence of many other metallic ions, *e.g.*, Ca^{++} , Mg^{++} , Zn^{++} , Pb^{++} , Ni^{++} , and Co^{++} (Menchutkin). Aluminum cannot be satisfactorily separated from iron by KOH if chromium is present. Like iron, non-volatile organic acids prevent the precipitation of the hydrous oxide of chromium by alkalis.

NH_4OH also precipitates a hydrous oxide, which even when freshly precipitated is only partially soluble in excess and is completely reprecipitated on boiling. The addition of NH_4Cl to a solution of an alkali chromite precipitates a hydrous oxide. The precipitate is soluble in HCl , a hydrous chloride being formed.

Chromium when present as compounds of CrO_3 forms with chlorine a brown volatile liquid, chromyl chloride CrO_2Cl_2 , boiling at about 118° .

The above brief outline of the chief chemical properties of chromium will serve as a foundation upon which to build our analytical procedures according to the nature of the problem in hand.

Preparation of the Material for Analysis. — (a)–The material is a green or violet-colored water-soluble salt or solution. Add a solution of KOH in excess until the precipitate first formed dissolves; boil. Decant, filter, or centrifuge; wash the precipitate and test for chromium as below.

(b)–The material is insoluble in water. Boil with concentrated

HNO_3 to which small amounts of KClO_3 are added from time to time. With few exceptions all chromium-containing compounds will pass into solution as chromates. Evaporate to dryness, carefully avoiding too high a temperature. Add HNO_3 and again evaporate; repeat if necessary so as to drive off all chlorine compounds; but if the material is to be converted into CrO_2Cl_2 the expulsion of Cl_2 is undesirable.

(c)–The material does not succumb to the treatment given in (b). Fuse the dry material with two or three times its volume of a mixture of Na_2CO_3 and KNO_3 (2 : 1). If chromium is present the fused mass will be yellow when cold (unless the color is masked by iron, manganese, vanadium, or other metals). Dissolve in cold water and filter or centrifuge. Chromium will be in the filtrate; iron and aluminum will be in the insoluble residue.

In the fusion there is apt to be a partial decomposition of the KNO_3 , and when the melt is dissolved in water the decomposition product reduces the yellow salt and the solution turns green. If the solution is distinctly green, complex ions will probably be formed and the subsequent reactions will be unsatisfactory. To obviate this difficulty it has been suggested that the fusing mixture consist of Na_2CO_3 and KClO_3 ; under these conditions all the chromium is oxidized to $\text{K}_2\text{Cr}_2\text{O}_7$. Great care must be used, for if mere traces of finely divided organic matter (dust) find their way into the molten KClO_3 a violent explosion may result.

(d)–Dry material containing chromium obtained by (b) or (c) is mixed with an equal volume of dry powdered NaCl and carefully heated in a crucible (Fig. 6, page 15) until perfectly dry. Pour over the residue about three times its volume of concentrated H_2SO_4 . Cover the crucible with a small object slide carrying a tiny hanging drop of dilute NH_4OH . Clamp the cover-slide tightly in place and heat carefully, tilting the crucible slightly from side to side with a rotary motion so as to cause the heavy CrO_2Cl_2 to rise. Allow to stand for a few minutes and heat again, raising the temperature to 115° – 118° . Repeat. If CrO_2Cl_2 has been formed and vaporized the hanging drop will contain $(\text{NH}_4)_2\text{CrO}_4$. Evaporate the drop, dissolve in water and test with AgNO_3 . The compound CrO_2Cl_2 can be obtained only when chromium is present as chromate, dichromate etc., *i.e.*, as compounds of the oxide CrO_3 . The cation Cr^{+++} (Cr_2O_3 (or CrO)) must first be converted to the anion (CrO_4^{--} , $\text{Cr}_2\text{O}_7^{--}$, etc.).

(e)—Separation of aluminum, iron and chromium, Riggs' Method. To the solution add one-tenth its volume of H_2O_2 and about one-tenth its weight of NaOH . Warm until effervescence ceases. Filter off or centrifuge the hydrous ferric oxide. Acidify the filtrate with acetic acid; hydrous aluminum oxide is precipitated. Filter or centrifuge. The clear solution contains the chromium as Na_2CrO_4 .

A—Detection by Means of Silver Nitrate — AgNO_3 .

Compound Formed — Ag_2CrO_4 or $\text{Ag}_2\text{Cr}_2\text{O}_7$.

The reagent is added by Method I to the test drop of material treated as directed above and acidified with HNO_3 . Dark red, highly pleochroic, crystals appear at once in the form of thin plates and scales with very irregular outlines, X's with sharply inclined dendritic cross bars, unsymmetrical crosses, very acute rhombs, rectangular and elongated six-sided plates. Well-formed crystals are seldom obtained; skeletal and dendritic forms are the rule (Fig. 170, page 327). The salt formed is probably $\text{Ag}_2\text{Cr}_2\text{O}_7$ when much HNO_3 is used, otherwise Ag_2CrO_4 (orthorhombic) is obtained.

$\text{Ag}_2\text{Cr}_2\text{O}_7$ and Ag_2CrO_4 can be recrystallized from NH_4OH or from hot HNO_3 . They can also be recrystallized from hot water, but the results are not so good; from neutral solutions the salt Ag_2CrO_4 , and not $\text{Ag}_2\text{Cr}_2\text{O}_7$, separates. From the ammoniacal solution a complex salt is obtained containing one or more molecules of NH_3 . This compound crystallizes in needles, skeleton crystals (X's) and aggregates resembling lichens.

Silver arsenate resembles silver chromate and bichromate both in color (but not in pleochroism) and in habit (Figs. 156, 157, page 311). The differences are sufficient, however, to enable the skilled analyst to distinguish between them. Silver vanadate (pyrovanadate) is yellow or orange colored (Fig. 110, page 181).

If much chlorine is present, as in testing the hanging drop in the CrO_2Cl_2 separation method, the addition of solid AgNO_3 (Method II) has much to recommend it. After all the chlorine has been precipitated as AgCl , the crystals of Ag_2CrO_4 make their appearance and can be readily distinguished with even much AgCl present. It is better, however, to decant just before the silver chromate begins to separate.

If the amount of CrO_4^{--} is small, add a very little H_2SO_4 to the

test drop before the addition of the AgNO_3 . Ag_2SO_4 is formed, into which the CrO_4^{--} enters in solid solution (isomorphous mixture) rendering the crystals of Ag_2SO_4 yellow or orange and pleochroic (Fig. 163, page 323). The sensitivity of the reaction is thus measurably increased, and the risk of mistaking it for arsenic or vanadium is obviated.

When the test drop contains ions forming compounds with silver which are insoluble in water acidified with HNO_3 , so dense a precipitate may be formed as seriously to mask the reaction for CrO_4^{--} . They may also completely precipitate the silver, leaving none to react with the chromate; due allowance should be made for such a contingency and there should be a second addition of AgNO_3 .

Experiments.

(a) — Dissolve a small amount of a chromium alloy in concentrated HNO_3 and KClO_3 as directed above in (b). Test for CrO_4^{--} with AgNO_3 .

(b) — Precipitate a chromate with AgNO_3 from neutral solution. Repeat, having HNO_3 present.

(c) — Recrystallize Ag_2CrO_4 from NH_4OH .

(d) — Precipitate with Ag^+ a chromate from a very dilute solution, in which a small amount of SO_4^{--} is present.

B-Detection by Means of Lead Acetate — $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$.

Compound Formed — PbCrO_4 .

To the test drop acidified with HNO_3 add the reagent by Method I, page 30.

Lead chromate separates in a very finely divided granular state, and no definite crystal forms are observable. The precipitate must be viewed by reflected light, for the test is based upon its bright yellow color, not upon crystal habit. Viewed by transmitted light, the bright yellow hue of the compound may not be recognized, especially when the precipitate is very small in amount.

This reaction for chromates should be regarded as supplementing and confirming the silver chromate test, for in the latter, as has been pointed out in A, the question always arises as to whether the crystals obtained with AgNO_3 are those of chromate, arsenate, or vanadate.

Since lead chromate is bright yellow, whereas lead arsenate and lead vanadate are white precipitates, the PbCrO_4 reaction may aid in clearing up any uncertainty in the silver test.

Strontium, barium, and zinc form yellow chromates of low solubilities in water, but since these chromates are soluble in HNO_3 they are not likely to interfere with the reaction nor to appear as precipitates. The same remarks apply with equal force to such of the rare earths as form difficultly soluble chromates.

Experiment.

(a) — Precipitate PbCrO_4 from very dilute solution.

C—Detection by the Chrome Alum Reaction.

Compound Formed — $\text{Cs}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$.

The test is performed exactly as indicated for Aluminum, page 162, observing all the precautions there indicated.

A hydrous oxide of chromium is obtained by precipitation with NH_4OH , decanting, filtering, or centrifuging. It is of even more importance than in the case of aluminum that an excess of H_2SO_4 shall be avoided. If the solution to be tested is yellow or red, acidify strongly with HCl , add a drop of alcohol and heat to boiling. Chromates, dichromates, and polychromates are thus reduced, and a green solution of chromium chloride will be obtained which can be precipitated by NH_4OH .

Every effort should be made to induce the octahedral crystals of cesium chrome alum to grow of sufficient size to exhibit their characteristic grayish violet color; for the test is not specific for chromium unless this can be done, but is common to a large group of "alum"-forming elements. (See page 155.) Nevertheless it is of value as a confirmatory test, particularly when obtained from a hydrous oxide precipitated from a green solution which in turn has been produced by the reduction of a yellow or red salt by alcohol.

Experiments.

(a) — Precipitate a hydrous oxide of Cr with NH_4OH , dissolve in a minimum of H_2SO_4 , and test with Cs_2SO_4 .

(b) — Convert CrCl_3 to the sulphate with H_2SO_4 , and test with Cs_2SO_4 . Complex ions will probably interfere.

D—Miscellaneous Confirmatory Tests.

(a)—Oxalic and oxalates give no precipitates with chromium compounds.

(b)—Potassium ferrocyanide gives no precipitate.

(c)—Potassium ferrieyanide changes chromates into chromic

salts. The same is true of potassium and ammonium thiocyanate.

(d)-Benzidine hydrochloride gives beautiful blue crystals with chromates, but this reaction is not due to chromium but is the result of an oxidation of the benzidine. Blue crystals are obtainable with any oxidizing agent behaving in solution in the same manner as chromates.

(e)-Chromates of the alkalis, of Mg^{++} , Ca^{++} , and Cu^{++} are soluble in water. The chromates of Tl^+ (Fig. 122, page 209), Sr^{++} , Zn^{++} , and Hg^{++} are slightly soluble. The chromates of Ag^+ , Ba^{++} , Hg^+ , Pb^{++} , Bi^{+++} , and Mn^{++} are insoluble or nearly so.

Bichromates are precipitated as chromates by Ag^+ , Ba^{++} , Hg^+ , Pb^{++} .

(f)-Disodium phosphate precipitates chromium phosphate, insoluble in acetic acid.

DETECTION OF MOLYBDENUM AND TUNGSTEN

These two elements resemble one another so closely and they so frequently occur in association that their microscopic identification in mixtures is likely to be difficult and uncertain.

Since they are weak bases they are seldom met with save as molybdates, tungstates, acid complexes, and in alloys or ores.

Before applying identity tests it is generally necessary to convert the material into alkali molybdates or tungstates, usually the "ortho" compounds. If a strong acid is added to a highly concentrated solution of these salts, molybdic acid or tungstic acid is precipitated; the former redissolves in excess of acid but the latter under favorable conditions of temperature (100°) and concentration separates as a yellow pulverulent precipitate. Since molybdic acid is white, the color change of tungstic acid from white $H_2WO_4 \cdot H_2O$ in the cold to yellow H_2WO_4 , when heated to boiling, has been suggested as a means of distinguishing between molybdenum and tungsten. Organic acids prevent the precipitation.

The addition of mineral acids to metatungstates (*e.g.*, $Na_2W_4O_{13} \cdot 10 H_2O$) does not cause a precipitate unless much acid is used and the preparation is heated to boiling for a considerable period;

the meta salt is then converted into the ortho salt, which in turn is decomposed and a yellow hydrated oxide is precipitated.

The most characteristic of their reactions is that of their alkali salts forming complex salts with phosphorus, arsenic and silicon, giving phospho-, arseno-, and silico-molybdates and tungstates, of the general formula $A_3RO_4 \cdot MoO_3 \cdot xH_2O$ or $A_3RO_4 \cdot WO_3 \cdot xH_2O$, where A may be any one of the alkalis or NH_4 , and R may be P, As, or Si. The insolubility of the ammonium phospho-complexes enables the easy separation of molybdenum and tungsten from mixtures containing them. It should be noted, however, that although we generally think of the insoluble complexes of molybdenum and tungsten as being those containing phosphorus, arsenic or silicon, as a matter of fact alkali molybdates (and to almost the same extent alkali tungstates) give rise to precipitates with nearly all other metallic salts.

A—Detection by Means of Dipotassium Phosphate — HK_2PO_4 .

Compounds Formed — $K_3PO_4 \cdot MoO_3 \cdot xH_2O$

$K_3PO_4 \cdot WO_3 \cdot xH_2O$.

To the dilute test drop strongly acidified with HNO_3 , a dilute solution of HK_2PO_4 is added by Method I. The phospho-complex is almost instantly formed. If after a few seconds no precipitate appears warm the preparation gently and set aside to cool for a few minutes. Examine with a magnification of about $200\times$. The precipitate is at first dense, heavy, and pulverulent; later the grains enlarge and appear more or less spherical; finally, very tiny isotropic octahedra are formed. The phosphomolybdate is yellow, but the phosphotungstate is white. When the amount of molybdenum or tungsten is very small, it is usually not possible to determine whether the precipitate is yellow or white. This test therefore must be regarded as a "group" rather than an "identity" test (Fig. 124, page 223).

The substitution of $H(NH_4)_2PO_4$ for the potassium salt gives less soluble complexes and increases the sensitivity of the reaction, but at the expense of the production of less distinctly crystalline precipitates.

B—By Means of Thallous Nitrate or Thallous Sulphate — TlNO_3 or Tl_2SO_4 .

*Compounds Formed — Tl_2MoO_4
 Tl_2WO_4 .*

To the test drop, which should not be too dilute and which has been made alkaline with NaOH , add the reagent by Method II, page 32, observing the caution there given to use a single large fragment.

Under the conditions as indicated above Tl_2MoO_4 is first precipitated as a dense white granular zone surrounding the reagent fragment; a few seconds later moss-like dendrites sprout from the fragment and grow to moderate dimensions; finally, beyond the non-crystalline zone first formed, there appear regular hexagons (Fig. 120, page 209), skeletons of hexagons, and irregular plates and scales. The hexagons, stars, and rosettes appear to be always small whether the solutions are dilute or concentrated.

Tl_2WO_4 does not usually develop the mossy dendrites, but instead forms a bristling coating of plates and scales in more or less dendritic aggregates upon the surface of the reagent. Like the molybdenum compound, the first result is an instantaneous white granular precipitate. In a few minutes there appear beyond this granular zone, groups of irregular, radiating, thin plates or scales terminating in acute angles resembling radiating masses or sheaf-like bundles of spear heads. Hexagons, stars and irregular plates are also formed (Fig. 121, page 209) similar to those of Tl_2MoO_4 , but the tendency to form individual hexagonal crystals is far less marked. The size and general appearance of the crystals of Tl_2WO_4 vary slightly according as ortho-, meta-, or para-tungstates predominate in the test drop — variations due to differences in the stability of the tungstates, and to their relative resistance to the action of the reagent. Tl_2WO_4 develops into larger crystals than Tl_2MoO_4 .

From dilute solutions these two salts separate so nearly alike in habit that only an experienced analyst can distinguish between them. From concentrated solutions the crystals are not well formed, but the chances for differentiation appear to be more favorable, especially if the coating upon the reagent is studied.

Vanadates give a white precipitate with a yellow or brown coating on the reagent fragment. Beyond the granular zone, stars and rosettes appear, but only after the test drop has evapo-

rated almost to dryness. The reagent fragment becomes covered with a mass of bristling crystals intermediate in form between Ti_2MoO_4 and Ti_2WO_4 , closely resembling the results obtained from a mixture of molybdates and tungstates.

The thallium reaction cannot be used to identify simultaneously molybdenum and tungsten when both are present, but can be used to advantage with pure tungstic or molybdic acids obtained by separating the two as described below.

Chromates give bright yellow Ti_2CrO_4 in fine needles, very slender prisms, or irregular groups and radiating masses of fine needles. The reagent fragment becomes covered with bristling hairs which later develop into acicular crystals. (Fig. 122, page 209.)

It must not be overlooked that TiNO_3 and Ti_2SO_4 yield salts of low solubility with many simple anions and complex ions. (See Thallium, page 167; see also Uranium, page 226).

C—By Means of Pyridine Hydrochloride and Ammonium Thiocyanate.¹⁰—To the test drop, concentrated with respect to molybdates, add a drop of HCl (1 : 4) and a rather large mass of pyridine hydrochloride. Allow to stand for a few seconds, then add a large fragment of NH_4SCN .

Salts of molybdenum and salts of MoO_4^{--} yield yellow and brown oily drops, but no crystals appear to be formed even when the preparation passes to dryness.

Allow the preparation to stand and to evaporate to dryness. Extract the dry residue with absolute alcohol. The alcoholic extract on evaporation leaves a non-crystalline brown residue. Add a very tiny drop of water or breathe upon the preparation. If molybdenum is present the brown compound is immediately changed into pink oily drops which, on standing, soon crystallize, giving rise to dendrites, plates, or tablets, X's, or to disks of radiating plates. These crystals are usually thin and appear to be faintly brownish when illuminated with ordinary transmitted light, but with polarized light they are extraordinarily pleochroic, the color changes being from a yellowish-brown or buff to an intense violet or purple (Fig. 125, page 223).

This reaction with pyridine hydrochloride, ammonium thio-

¹⁰ Martini's reagent, modified. *Mikrochemie* 7, 30 (1929).

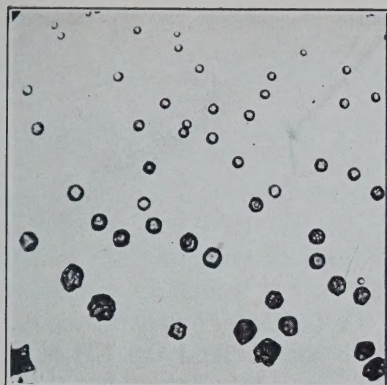


FIG. 124. Molybdenum (MoO_4^-) with Dipotassium Phosphate. 200X.



FIG. 125. Molybdenum (MoO_4^-) with Pyridine Hydrochloride and Ammonium Thiocyanate. 200X.

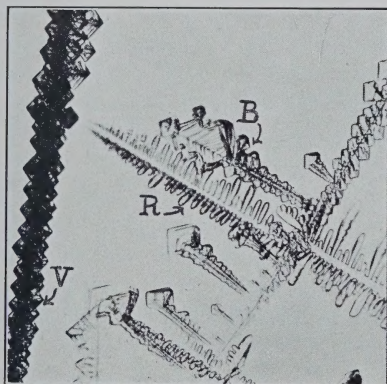


FIG. 126. Cobalt with Pyridine Hydrochloride and Ammonium Thiocyanate. 70X.

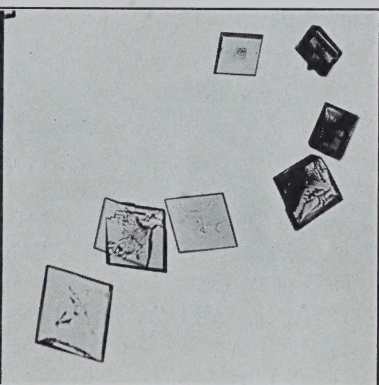


FIG. 127. Cobalt with Pyridine Hydrochloride and Ammonium Thiocyanate. 100X.

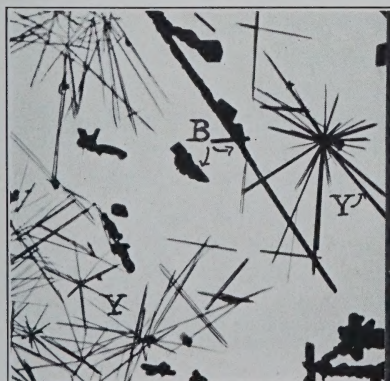


FIG. 128. Copper with Pyridine Hydrochloride and Ammonium Thiocyanate. 50X.

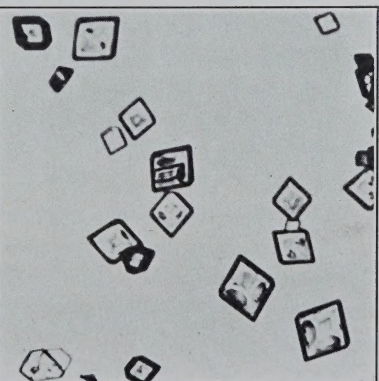


FIG. 129. Uranium (UO_2^{++}) with Thallous Nitrate and Ammonium Carbonate. 200X.

cyanate, and polarized light, though not very sensitive, appears to be specific for molybdenum.

In hot weather or a very hot room it is difficult to obtain characteristic crystals. Chilling the preparation by laying it upon a cold metal surface will induce crystallization of the pink oily drops.

Tungsten gives no reaction. Zirconium, titanium, vanadium (and tungsten) do not interfere. Vanadium salts and vanadates, however, usually give a faint bluish zone around the NH_4SCN fragment and also yield yellow and brown oily drops; but these droplets are not convertible by water into a colored strongly pleochroic compound.

For reactions obtainable with other elements see Cobalt, page 242.

D-Separations and Confirmatory Reactions.

(a)-Separation of W from Mo and Te.¹¹ — The hydrous oxides obtained from sulphides or by other means are dissolved in aqua regia and are evaporated with concentrated HCl substantially to dryness. This dehydrates the tungstic acid and renders it insoluble in 2 N HCl. Boiling the residue with acid of this strength dissolves molybdenum, vanadium and tellurium. From the solution tellurium can be precipitated by zinc and HCl.

(b)-Dissolve the dehydrated H_2WO_4 (obtained as described above) in NH_4OH , evaporate almost to complete dryness, cover with a drop or two of SnCl_2 ; a flocculent deep blue compound is obtained — $\text{W}_2\text{O}_5 \cdot x\text{WO}_3$.

(c)-To the HCl extract from the method of separation (a), add KSCN and metallic zinc. If molybdenum is present the solution turns a deep red, not destroyed by H_3PO_4 (distinction from iron). Tungstates give a similar reaction.

(d)-To the solution acidified with HCl add a fragment of $\text{K}_4\text{Fe}(\text{CN})_6$.

Mo. The fragment becomes surrounded by a deep brown jelly-like colloidal mass; at a distance from the reagent the brown compound becomes curdy, and yet farther away, granular.

¹¹ Noyes and Bray: *Qualitative Analysis for the Rare Elements* (Macmillan, New York, 1927), p. 74.

W. Usually little action until warmed, then a brown colloid is formed, less jelly-like than in the case of Mo.

The brown compound is soluble in NH_4OH and also in NaOH . Distinction from U and Cu.

(e)–Solutions containing Mo or W, acidified with HCl and treated with metallic Zn give a blue solution; but in the case of Mo the solution does not remain blue, but finally becomes brown.

DETECTION OF URANIUM

The element uranium, although falling in the same vertical group as molybdenum and tungsten, has little in common with them micro-analytically, but presents certain analogies with chromium. Uranium functions chiefly as a base and forms few compounds in which it acts as an acid. The uranates are weak compounds which are easily decomposed.

The tests for uranium are based upon the assumption that either uranyl nitrate or uranyl acetate has been produced and is present in the test drop.

A–Detection by Means of Sodium Acetate and Zinc Acetate.

Compound Formed — $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$.

At the corner of an object slide dissolve in dilute $\text{HC}_2\text{H}_3\text{O}_2$ a very little $\text{NaC}_2\text{H}_3\text{O}_2$ and about twice as much $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$. Mix thoroughly by stirring and carefully evaporate to dryness so as to obtain a thin uniform film. Place near the dry film a drop of the material believed to contain uranium, acidify with $\text{HC}_2\text{H}_3\text{O}_2$, mix and draw the solution in a narrow streak across the dry film. (Method III, page 34.)

If uranium is present, there will be formed tetrahedra of sodium uranyl acetate and octahedra-like, monoclinic, polysynthetic twins of sodium zinc uranyl acetate. The characteristics of these two salts have been discussed at length under Sodium, page 52 (Figs. 28, 30, 31, page 53).

The reaction is peculiar to uranium and is subject only to the sources of error due to the precipitation of uranium in insoluble form, as stated under Sodium.

B-Detection by Means of Thallous Sulphate — Ti_2SO_4 — in a Solution Containing Ammonium Carbonate.*Compound Formed* — $2 \text{Ti}_2\text{CO}_3 \cdot (\text{UO}_2)\text{CO}_3$.

This reaction, according to H. Behrens, is much more sensitive than that given above. We have, however, found it always difficult to obtain, save when dealing with comparatively pure uranium products and under rather carefully controlled conditions. Moreover, the crystals are very tiny and require a high power to resolve them.

To the solution to be tested NH_4OH is added and the precipitate thus produced is separated by filtration or by the centrifuge, and is dissolved in a strong solution of ammonium carbonate. To this ammoniacal solution a fragment of thallous sulphate or thallous nitrate is added. As in substantially all cases where Ti_2SO_4 or TiNO_3 are used as reagents, the reagent fragment first becomes coated with a drusy layer of the double salt, and it is only after a few minutes that a zone of free crystals can be observed at a short distance from the reagent. The tiny crystals are probably orthorhombic and take the form of rhombic plates and more or less irregular three-, four-, and six-sided tabular crystals or crystalline grains (Fig. 129, page 223).

There appears to be some confusion as to the true nature of the salt which separates. Some investigators have ascribed to it the formula $\text{Ti}_2\text{SO}_4 \cdot (\text{UO}_2)\text{SO}_4 \cdot 2 \text{H}_2\text{O}$,¹² but since crystals of identical habit are obtained whether Ti_2SO_4 or TiNO_3 is used as the reagent it seems reasonable to consider that H. Behrens' formula $2 \text{Ti}_2\text{CO}_3 \cdot (\text{UO}_2)\text{CO}_3$ is correct.

Since the crystals are minute and their habit not readily discerned, and since thallous compounds are precipitated by so many different ions, the confirmatory test suggested by Behrens should never be omitted. To this end, decant the mother liquor and flood the precipitate with a solution of $\text{K}_4\text{Fe}(\text{CN})_6$ in acetic acid. If the precipitate consists of a salt of uranium, a brown precipitate results. This should make the test conclusive, providing copper has been proved to be absent.

¹² W. Behrens: *Tabellen*, p. 203.

H. Behrens: *Anleitung*, p. 123.

Miscellaneous Reactions.

(a)–With oxalic acid or oxalates: Separation of $\text{UO}_2 \cdot \text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ in very pale yellow orthorhombic prisms and plates, the latter thin, rectangular or square (See page 110).

(b)–With alkali hydroxides or ammonium hydroxide basic uranates are precipitated $((\text{UO}_2)_2\text{O} \cdot (\text{OM})_2)$ insoluble in excess of the reagents, but readily soluble in $(\text{NH}_4)_2\text{CO}_3$.

DETECTION OF SULPHUR, SELENIUM AND TELLURIUM

Free sulphur can be recognized by its physical properties, behavior on heating and by its crystal form, orthorhombic (or monoclinic), as it separates from solvents such as CS_2 , CCl_4 , CHCl_3 , C_6H_6 .

Loosely bound sulphur in sulphides can be detected by its reaction with alkaline sodium nitroprusside and by evolution of H_2S when treated with dilute HCl . The sulphur in these compounds can also be oxidized to sulphate by exposing them in an aqueous hanging drop to the action of bromine vapors in a microcrucible.

The detection of the various acids of sulphur will be found under their proper designations in the discussion of the anions (pages 321–335).

Since most selenites and selenates are isomorphous with their corresponding tellurites, tellurates, and sulphates, it is always necessary to prove the absence of selenium and tellurium before there can be any certainty regarding the presence of the sulphur-containing anions.

The detection of selenium and tellurium is based upon the ease with which they are reduced to the “metallic” state, and that when finely divided their colors are very different.

Most tellurium compounds differ in their chemical behavior sufficiently from those of sulphur and selenium so that there is little danger of confusion; but between certain compounds of sulphur and selenium there is such a close resemblance as to necessitate care on the part of the analyst if he wishes to avoid errors.

The only selenites and tellurites which are likely to be met with in qualitative analysis and which are soluble are those of the alkalis.

Selenates and tellurates are sometimes (though rarely) met with in the routine examinations of an analytical laboratory, but more frequently the problems will be the detection of selenides, or tellurides in ores, or the free elements as patinas upon the surfaces of alloys.

A-Detection of Selenium by Means of Hydroxylamine Hydrochloride — $\text{NH}_2\text{OH}\cdot\text{HCl}$.

Compound Formed — Se.

To a drop of the NaOH or HCl solution of the material to be tested several fragments of citric acid are added, and the preparation stirred until the citric acid has dissolved. If a precipitate occurs add more acid until a clear drop has been obtained. A fragment of hydroxylamine hydrochloride is now added. If selenium is present there will form around the fragment of reagent a brown ring. In a very short time a precipitate of bright red selenium takes place. The preparation must be viewed by reflected light. Whether the precipitate be red, brown or black, it consists of selenium, for it has been shown¹³ that in the presence of citric acid no tellurium is precipitated. Traces of selenium in the presence of tellurium can be detected by this method.

In the absence of any precipitation of selenium the preparation can be tested for tellurium by adding a drop or two of HCl (1 : 4) and a fragment of metallic zinc. Tellurium is precipitated in a dense black granular or flocculent zone about the zinc, but not clinging to the fragment as "trees" do.

If the material is suspected of being a salt of acids of sulphur, selenium, or tellurium, the test can be applied direct, but in very complex material it is wise to precipitate the selenium or (and) tellurium by means of SO_2 in HCl, in cold, or warm but not hot, solutions.

The necessity for an examination by reflected light has been mentioned above; this is essential since in concentrated solutions the reagent often becomes covered with a dense white coating, which, as it falls off and becomes peptized, appears brown by transmitted light if sufficiently finely dispersed, or if the white precipitate scatters the light it will appear black, in either case leading to a false conclusion on the part of the analyst.

¹³ Lehner and Kao: *Jour. Amer. Chem. Soc.* **47**, 2454 (1925).

B—Detection of Selenium and Tellurium by Means of Hydroquinone¹⁴ — $C_6H_6O_2$.*Compound Formed* — Se; Te.

The material to be tested is dissolved in concentrated HNO_3 and evaporated to dryness at the corner of an object slide. The dry residue is covered with one or more drops of moderately concentrated H_2SO_4 and heated until fumes of SO_3 appear. Treat again with H_2SO_4 and decant from any insoluble precipitate. The decanted solution is evaporated until SO_3 fumes are formed. Cool the preparation. (Before the preparation has completely cooled, it should be examined for crystals of $2 TeO_2 \cdot SO_3$ which may have been formed.) Place a drop of a saturated solution of hydroquinone in concentrated H_2SO_4 adjacent to the test drop and cause it to flow into the test drop. *Warm gently*. Selenium is precipitated brown or red.

Under the conditions of the test as given above tellurium is not reduced until the temperature is raised to the point when SO_3 fumes are formed. If therefore no selenium has been precipitated the preparation is heated until SO_3 is evolved. Cool and examine under the microscope. Tellurium separates in very slender, black, acicular crystals, in sheaves, irregular bundles, and in aggregates forming crosses or radiating masses.

If much selenium is present the selenium precipitate obscures the crystals of tellurium. Both selenium and tellurium are, however, precipitated separately and can usually be distinguished one from the other. Decanting after the separation of the selenium and before fuming off the SO_3 is always advisable.

When tellurium is present in appreciable amount, it is possible to obtain an identity test for this element prior to the addition of the hydroquinone. If the cooled test drop is examined, there will be seen masses of thin colorless plates grouped in malformed irregular rosettes with many petals; there are also formed bundles of plates on edge resembling sheaves of acicular crystals. The compound is probably $2 TeO_2 \cdot SO_3$; ¹⁵ its appearance is characteristic and seems to be specific for tellurium, but under certain conditions bismuth salts heated with concentrated H_2SO_4 give rise to crystals which may puzzle the inexperienced analyst. It is essential that the preparation be examined promptly under the micro-

¹⁴ Putnam, Roberts and Selchow: *Amer. Jour. Sci.* **15**, 257 (1928).

¹⁵ Putnam, Roberts and Selchow: *loc. cit.*

scope before it has become thoroughly cold, for the crystals redissolve in the water absorbed from the air by the H_2SO_4 .

Miscellaneous Reactions of Selenium and Tellurium.

(a)—Solutions of selenium and tellurium compounds in HCl are reduced by SO_2 to Se and Te if SO_2 is in large excess, but if SO_2 is insufficient to cause complete reduction selenium monochloride is formed, and can be distilled off in a pure state.¹⁶

This separation can be practiced in the micro-crucible with a hanging drop.

(b)—Selenium and tellurium are strongly electro-negative; elements more electro-positive than Se or Te will therefore reduce their compounds and precipitate them in a finely divided condition — red, brown, or gray in the case of Se ; gray or black in the case of Te .

(c)— FeSO_4 in *concentrated* HCl at room temperature reduces selenates but not tellurates, but Te is precipitated if *dilute* HCl is used; the same is true with Na_2SO_3 .

(d)— SnCl_2 in HCl solution reduces both Se and Te if the preparation is warmed. (See Mo and W .)

(e)— SeO_2 sublimes at 200° , but TeO_2 fuses at a red heat and is volatilized only at high temperatures.

¹⁶ Lehner and Kao: *Jour. Amer. Chem. Soc.* **47**, 769, 2454 (1925).

CHAPTER IX

DETECTION OF THE ELEMENTS OF GROUP VII

F; Mn; Cl, Br, I

Group VII consists of the transitional element fluorine; the sub-group chlorine, bromine, and iodine; and the elements manganese and rhenium.

There are but few analytical analogies in Group VII that need occupy our attention.

Fluorine stands practically alone. It will be met with in the form of fluorides or fluorine-containing complexes. From these the fluorine is liberated by strong acids, and in the presence of silicon and sodium forms characteristic sodium fluosilicate whose behavior and properties have been discussed under Sodium, page 63. (See also Detection of Anions.)

Manganese resembles its horizontal analogue iron in Group VIII, especially in its bivalent sulphate and double sulphates. Its analogy to chlorine is well marked in the isomorphism of alkali permanganates and alkali perchlorates; advantage of this is taken in the detection of ClO_4^- and also of members of the potassium group.

Chlorine, bromine and iodine form a triad of probably the most closely related elements in the Periodic System. Not only are they closely related in the habit of their many commonly met with salts, but their analytical behavior is such as to require great care when dealing with mixtures in which two or more of the halogens are present.

The halogen salts of the alkalis comprise the vast majority of the isotropic salts with which the analyst comes in contact.

Since the detection of chlorine, bromine, and iodine involves the detection of halides and halates, the consideration of the analytical procedures to be followed will be found under the designation of these anions. (See pages 340-357).

DETECTION OF MANGANESE

A—By Means of Oxalic Acid — $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$.*Compound Formed* — $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$.

This reaction is applicable only to manganous salts in a moderately pure state, but under favorable conditions it is sensitive and characteristic.

The most reliable procedure is as follows. Prepare upon an object slide a dry film of oxalic acid, or better, one of acid potassium oxalate (See Method III, page 34). Place adjacent to the reagent, a drop of the moderately dilute neutral (or at the most only faintly acid) solution of the material to be tested. Draw a narrow streak of the test drop across the reagent film.

Manganous oxalate, $\text{MnC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$, separates in large colorless six-armed radiates built up by the crossing of long thin twinned prisms with acute or truncated ends. These prisms are strongly birefringent, with parallel extinction, and exhibit very beautiful polarization colors (Fig. 69, page 109). Highly refractive crystal-line grains and pseudo-octahedra may also be formed.

The test fails in the presence of an excess of ammonium salts, when an appreciable amount of a mineral acid is present, or if free strong organic acids are present. Very dilute acetic acid or a slightly ammoniacal reaction has no injurious effects.

The test may be masked by elements forming insoluble or difficultly soluble oxalates, particularly those to be found in Group II and in Group VIII. (See page 110.)¹

Experiments.

(a) — Test as above MnSO_4 . Then try the addition of a drop of $\text{H}_2\text{C}_2\text{O}_4$ to a test drop, by Method I.

(b) — Try the effect of free acids upon the test.

B—By Means of Disodium Phosphate — HN_2PO_4 .*Compound Formed* — $\text{NH}_4\text{MnPO}_4 \cdot 6 \text{H}_2\text{O}$.

This test for Mn^{++} is performed in a manner similar to that used for the detection of magnesium (See pages 77, 121) save that no citric acid is added.

To the test drop add a *trace* of HNO_3 , then a very little NH_4Cl and a fragment of HN_2PO_4 . Stir thoroughly until well mixed

¹ See also Schoorl: *Beiträge*, p. 107.

Wagenaar: *Pharm. Weekblad* **49**, 14 (1912); *Chem. Abs.* **6** (1), 724 (1912).

and the phosphate is all dissolved. Cause a drop of strong NH_4OH to flow into the prepared test drop. Crystals identical in appearance and isomorphous with those of $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ are formed. To confirm the reaction, decant the mother liquor, cover the crystals with a drop of NH_4OH , and add a drop of H_2O_2 . Warm gently; the crystals turn brown if manganese is present.

Experiment.

(a) — Precipitate $\text{NH}_4\text{MnPO}_4 \cdot 6 \text{H}_2\text{O}$, as directed above. Treat with H_2O_2 .

C—By Means of Potassium Chromate — K_2CrO_4 .

Compound Formed — Manganous chromate of variable composition.

To the neutral or alkaline moderately concentrated test drop apply the reagent K_2CrO_4 by Method II, page 32. Tiny granules at first appear which grow into groups, masses, sheaves, and radiating aggregates of yellowish brown, strongly pleochroic, acicular crystals (Fig. 123, page 209).

The test drop should be neutral or slightly alkaline, and more than a mere trace of free HNO_3 retards the separation of the crystals and greatly alters the crystal habit. Instead of fine acicular crystals, dendritic masses of stout yellowish-brown prisms are obtained. Other strong mineral acids have a like effect.²

$\text{K}_2\text{Cr}_2\text{O}_7$ applied as above gives no crystalline precipitate.

Ag^+ , Pb^{++} , Tl^+ , Hg^+ , Hg^{++} , Zn^{++} , Ba^{++} , Sr^{++} mask or interfere with the reaction.

Experiments.

(a) — Test a drop of MnSO_4 with K_2CrO_4 ; with $\text{K}_2\text{Cr}_2\text{O}_7$.

(b) — Repeat the test in a solution slightly acid with HNO_3 .

D—Detection of Manganese Irrespective of its State of Oxidation.

(a)—*By Fusion with Alkali Carbonates.* — The fusion can be performed upon platinum foil or in a tiny platinum cup. First fuse a mixture of Na_2CO_3 with a very little KNO_3 , using as small an amount as possible at the corner of the tipped-up foil. Add

² For a critical discussion of this test for manganese, see Wagenaar: *Pharm. Weekblad* 49, 14 (1912).

the finely powdered substance, a very little at a time, to the fused alkali, heating after each addition until each portion has passed into combination and a clear melt results. The quantity of the substance to be tested that it is necessary to add will necessarily depend upon the amount of manganese present.

Manganese fused with alkali carbonates gives an alkali manganate intensely green in color. The green color is even more marked when the melt is moistened with water. This color reaction is doubtless the most sensitive and specific of the tests at our command.

Often by carefully acidifying the alkaline solution with H_2SO_4 the green manganate Na_2MnO_4 is converted into pink permanganate NaMnO_4 , and this in turn is decomposed with the precipitation of a hydrated oxide of manganese.

Iron and chromium may completely mask the reaction; for this reason it is better practice first to precipitate the manganese as a hydrous oxide and use this precipitate for the fusion test.

Experiment.

(a) — Oxidize MnSO_4 to manganate, by fusion. Acidify, and precipitate KClO_4 in the solution.

(b) — *Precipitation of Manganese as Mn_3O_4 (?)*. — The precipitation of a brown or black oxide, probably hydrated, can generally be accomplished by several methods. The solution to be tested is made strongly ammoniacal, H_2O_2 added and the mixture boiled. A brown hydrated peroxide is precipitated. In the absence of cobalt (and nickel) this reaction is characteristic of manganese. Cobalt gives a precipitate indistinguishable from that of manganese. Filter or centrifuge; dry the precipitate and fuse with alkali as above.

The precipitation of an oxide of manganese by H_2O_2 is a valuable means of separating manganese from other elements, both for the purpose of identifying manganese and also to remove manganese before testing for other ions with whose detection manganese might interfere.

Manganese can also be separated by adding KClO_3 to a solution in moderately concentrated HNO_3 and boiling; dark brown MnO_2 (?) is precipitated, which can be filtered off, or centrifuged, and a confirmation test for manganese applied. Cobalt may yield a similar brown precipitate.

(c)—*By Conversion into Permanganic Acid* — $HMnO_4$.

1—*Oxidation by Means of Sodium Bismuthate*. — Dissolve the material in concentrated HNO_3 and evaporate the solution to dryness. Treat the residue with concentrated HNO_3 and again evaporate. Dissolve the residue in HNO_3 and add sodium bismuthate in very small portions at a time, stirring after each addition and allowing the preparation to stand for a short time after each addition. A pink or purple color ($NaMnO_4$) indicates manganese. Too high a concentration of manganese interferes.

If a brown precipitate results but no pink color, proceed as follows. Add very carefully the smallest possible fragment of sodium thiosulphate, stir and allow to stand, then repeat the process until substantially all the oxide of manganese has been dissolved, but there must be no excess of $Na_2S_2O_3$. To the colorless milky drop add one or two small drops of dilute HNO_3 (1 : 4) and stir very carefully. Again add very slowly and cautiously sodium bismuthate. A pink or purple color indicates manganese. Add a little KCl and a tiny drop of $HClO_4$. The crystals of $KClO_4$ take up the permanganate and become colored pink. This test is specific for manganese.

2—*Oxidation by Means of Ammonium Persulphate*.³ — Dissolve the material in HNO_3 , evaporate to dryness. Treat with concentrated HNO_3 and again evaporate. Repeat this treatment several times to insure the removal of halogens. Dissolve the residue in dilute HNO_3 . Add a *very tiny* fragment of $AgNO_3$ (as a catalyst) and a moderate-sized fragment of $(NH_4)_2S_2O_8$. Warm gently and allow to stand. A pink or purple color indicates manganese.

In both the (1) and (2) procedures much depends upon the performance of the test slowly and carefully. If no positive results are obtainable it is wise to repeat the test varying the concentrations.

In the experience of the authors oxidation with sodium bismuthate is more reliable in the hands of inexperienced analysts than is oxidation with persulphates.

Experiments.

(a) — Oxidize $MnSO_4$ to permanganate, by means of sodium bismuthate. Test with $KClO_4$.

(b) — Oxidize $MnSO_4$ with $(NH_4)_2S_2O_8$ and test as above.

³ Putnam, Roberts and Selchow: *Amer. Jour. Sci.* **15**, 261 (1928).

CHAPTER X

DETECTION OF THE ELEMENTS OF GROUP VIII

Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt
(Cu, Ag, Au)

In Group VIII are found the elements forming the ends of the three long horizontal periods of the Periodic System and therefore a group of elements whose properties are in a large measure transitional between Groups VI and VII and Group I.

In Group VIII a basic character is again in the ascendency, in most cases completely submerging acidic properties. Of the acidic properties there remain but the vestiges to be found in the composition of some of the oxides and in the formation of unstable alkali ferrates, ruthenates and osmates (*e.g.*, K_2FeO_4 , K_2RuO_4 , K_2OsO_4). These compounds correspond to the analogous molybdates, tungstates, chromates, and manganates and in general comport themselves in like manner. Of these acidic forms, the only ones likely to be encountered in qualitative chemical analysis are ruthenium red and osmic acid.

In Group VIII the close analogies between the elements are to be found in the horizontal lines rather than in the vertical, and the sub-groups which interest the analyst are sub-divisions horizontally instead of vertically; that is to say, that iron, cobalt and nickel resemble each other more closely than do iron, ruthenium and osmium. So too, rhodium behaves more like palladium than like cobalt or iridium, and palladium forms salts which react more like those of rhodium than like similar salts of nickel or platinum; the resemblance to nickel is, however, apparent in the formation of a difficultly soluble glyoxime.

Vertical analogies hold to a limited degree, however, and the analyst is confronted with a dual grouping not marked in the other main groups of the Periodic System. He must also bear in mind the transitional character of the members of Group VIII as exemplified in the series Cr, Mn, Fe, Co, Ni, Cu; Mo, Ru, Rh, Pd, Ag; and W, Os, Ir, Pt, Au.

Another characteristic not to be forgotten is that the similarities in the properties of the elements in the horizontal long periods hold for the next horizontal long period above or below, but there is little analogy with the nearest elements in the horizontal short periods.

Group VIII taken as a whole is characterized by the marked tendency with which its members unite with acidic elements to form *complex anions*. In these stable complexes the specific reactions of the individual elements are lost and a characteristic reaction for the complex ion must be sought, or the complex must be completely destroyed by ignition, fusion, or the action of a powerful decomposing agent.

The salts of the elements of Group VIII offer many striking analogies with those of other elements in the horizontal long periods. These analogies can be readily understood by reference to tables of optical properties. For example, monoclinic $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ is isomorphous with monoclinic $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$. Triclinic $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ if crystallized in the presence of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ becomes monoclinic. Orthorhombic $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ in the presence of monoclinic $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ becomes monoclinic. On the other hand, monoclinic $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ in the presence of orthorhombic $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ becomes orthorhombic. A great variety of solid solutions are thus possible, and it is probably not far from the truth if we say that the sulphates of iron, cobalt, nickel, manganese, magnesium, and zinc can form isomorphous mixtures. All of these elements also form monoclinic hexahydrated double sulphates of the general formula $M_2\text{SO}_4 \cdot N\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ where M is an element of the potassium group and N one of the elements just referred to.

The bivalent compounds of iron, cobalt, and nickel corresponding to the formulas FeX_2 , CoX_2 , and NiX_2 closely resemble like compounds of chromium, manganese, and copper, and also to a certain degree those of magnesium, cadmium, and zinc.

FeX_3 is analogous to AlX_3 , CrX_3 , and MnX_3 , and in most cases the salts are isomorphous. A further resemblance of Fe^{+++} to Al^{+++} , Mn^{+++} , and Cr^{+++} is seen in the formation of ferric alum.

Both iron and cobalt unite with other elements to form complex ions, but this property is much less marked in nickel. A further similarity between iron and cobalt is to be found in the formation

of stable bivalent and trivalent compounds, whereas nickel forms almost exclusively compounds in which it is bivalent.

Cobalt and nickel (and copper) differ from iron in their reactions with NH_4OH and with $(\text{NH}_4)_2\text{CO}_3$, for easily soluble ammonia compounds are formed, whereas in the case of iron an insoluble hydrous oxide is precipitated.

The most frequently encountered complex ions in which iron enters are $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, corresponding to which are $\text{Co}(\text{CN})_6^{4-}$ and $\text{Co}(\text{CN})_6^{3-}$, but cobalt forms in addition a very large number of complex ions of which the most striking are those in which NH_3 enters. All these complexes are of extreme importance, for it is not possible to detect directly iron or cobalt in them, nor to obtain a reaction for CN^- in the complex by ordinary methods of procedure. Similar conditions obtain in other complex ions of iron and of cobalt.

As regards the relations of the secondary sub-group of Group I to Group VIII little more need be added to the comments which have already been made.

Copper, like cobalt, forms a double thiocyanate with mercury. Silver falls in one of the horizontal short periods, and therefore has substantially nothing in common with the elements in the horizontal long periods.

Gold, in the third horizontal long period, is best grouped with osmium, iridium, and platinum, and like these elements enters into the formation of complex ions.

Since copper, silver, and gold fall in alternate horizontal short periods these three elements have no micro-analytical analogies and do not interfere with one another in the tests applied for their detection.

DETECTION OF IRON

A—By Means of Potassium Ferrocyanide — $\text{K}_4\text{Fe}(\text{CN})_6$.

Compounds Formed — $\text{Fe}_4(\text{Fe}(\text{CN})_6)_2$ or
 $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$.

To the test drop acidified with HCl add a little powdered $\text{K}_4\text{Fe}(\text{CN})_6$. A dark blue precipitate or color indicates iron.

Copper and uranium give dark brown ferrocyanides with $\text{K}_4\text{Fe}(\text{CN})_6$, and if present in high percentages may completely

mask the reaction for iron by preventing the recognition of a blue coloration. Gallium gives a white gelatinous precipitate.

The reagent must always be present in considerable excess, for difficultly soluble ferrocyanides are formed with many other elements and there must be sufficient $\text{Fe}(\text{CN})_6^{4-}$ ions to react with all precipitable cations. Most of these insoluble ferrocyanides are white or only faintly colored, but may so dilute the blue color of the iron compound as to cause it to be overlooked.

The test should be made at room temperature, for if the reagent is added to a hot strongly acid test drop there may be sufficient decomposition of the $\text{K}_4\text{Fe}(\text{CN})_6$ to give a blue color even in the absence of iron.¹

The reaction is best performed upon material which has been evaporated to dryness with concentrated HNO_3 in order to convert the iron into the ferric condition. Under these circumstances flocculent, dark blue, very insoluble ferric-ferrocyanide $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ is precipitated.

$\text{K}_4\text{Fe}(\text{CN})_6$ produces a dark blue precipitate with ferrous salts as well as with ferric, but under certain conditions the $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ may be peptized and a blue solution may result.

$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ is soluble in solutions of the fixed alkalis and is reprecipitated by HCl .

To obtain the best results the $\text{K}_4\text{Fe}(\text{CN})_6$ should be dried until anhydrous and finely powdered, and a small quantity of this reagent added to the test drop.²

A somewhat more convenient and sensitive reagent can be prepared by incorporating $\text{K}_4\text{Fe}(\text{CN})_6$ in a fiber such as cotton or viscose rayon.³ The test drop should be of small diameter and the fiber when applied should have at least half its length outside the drop for the reason that the best reaction is obtained where a film has been drawn by capillarity around the fiber. The preparation is allowed to evaporate spontaneously to dryness and the fiber examined under the microscope. Applied in this manner the test is generally free from interferences.

¹ Putnam, Roberts and Selchow: *Am. Jour. Sci.* **15**, 424 (1928).

² Behrens: *op. cit.*, p. 26.

Behrens-Kley: *op. cit.*, p. 23.

³ Mayrhofer: *op. cit.*, p. 92.

Experiments.

- (a) — Test for Fe in simple salts.
- (b) — Test in mixtures with other elements which will be precipitated by $K_4Fe(CN)_6$.
- (c) — Test for iron in a ferrocyanide, by first decomposing the complex by ignition. Use Method B.

B—By Means of Potassium Thiocyanate — KSCN.

Compound Formed — $Fe(SCN)_3$.

The iron must be in the ferric condition. It is therefore best to treat the material with concentrated HNO_3 and evaporate to dryness. HCl is added and the preparation is again evaporated to remove HNO_3 . The residue is dissolved in water, acidified with HCl and a relatively large fragment of $KSCN$ is added. If iron is present, a pink or red coloration is produced; the intensity of the color varies with the amount of iron present.⁴

Oxides of nitrogen must be absent, otherwise a red color may be obtained in the absence of iron.

$HgCl_2$ and a number of analogous salts discharge the red color, hence such interfering substances must be absent.

Molybdates in the presence of strong reducing agents give a red color with $KSCN$. This source of error is eliminated if oxidation with HNO_3 has been followed as directed above.

$KSCN$ gives precipitates with salts of a number of elements. An excess of the reagent must therefore always be present if a satisfactory reaction for iron is to be obtained. When the precipitate of a white thiocyanate is a heavy one the intensity of the coloration of the $Fe(SCN)_3$ may be misjudged; in the face of such a condition, filter or centrifuge, add more $KSCN$, and if the color is not distinct examine by the capillary tube method.

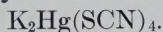
The test may also be made by applying a viscose-rayon fiber which has been impregnated with $KSCN$, the application being made as outlined under the $K_4Fe(CN)_6$ method on page 239. When using $KSCN$ fibers it is essential that the observations shall be made on the treated fiber outside the circumference of the drop. If more than mere traces of iron are present the fiber will appear black.

⁴ If no color is visible in the test drop, Putnam, Roberts and Selchow: *op. cit.*, suggest taking up the drop in a thin-walled capillary tube and examining it on a pure white background in a good light. Under the latter procedure a very faint pink can be more readily perceived.

If no well-marked reaction is obtained with KSCN, but a strong one with $\text{K}_4\text{Fe}(\text{CN})_6$, the iron is chiefly in the ferrous condition; but if both reactions are well defined, it is not possible to determine whether ferrous compounds are present or absent. Under these conditions test with $\text{K}_3\text{Fe}(\text{CN})_6$.

DETECTION OF COBALT

A—By Means of Potassium Mercuric Thiocyanate —



Compound Formed — $\text{Co}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$.

The material is prepared for analysis by treatment with HNO_3 as discussed under Zinc, page 124, and Copper, page 249.

Add the reagent by Method I or Method II, but better results are obtainable if Method III is used.

$\text{Co}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ separates in dark blue rectangular or tapering prisms, singly, or more often in many-armed radiates (Fig. 79, page 125). The reaction is specific though not very sensitive. The cobalt double thiocyanate is more soluble than those of zinc or copper and will not separate at once but appears after a few seconds. The influence of the presence of large amounts of zinc, cadmium, copper, and iron has been discussed at length under Zinc, page 129.

The cobalt mercury thiocyanate salt often forms metastable solutions from which it is difficult to induce the separation of characteristic crystals.

Nickel in very concentrated solutions gives tiny spherulites or disks of very fine needles. A great excess of nickel may prevent the formation of the cobalt salt.

Experiment.

See Zinc, Method A, page 124.

B—By Means of Potassium Nitrite — KNO_2 .

Compound Formed — $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot 1\frac{1}{2} \text{H}_2\text{O}$.

To the neutral very dilute test drop add a fragment of KNO_2 ; stir until dissolved. Warm and while still warm add a drop of acetic acid. Any Co^{++} present is converted into Co^{+++} and unites with NO_2^- to form the complex ion $\text{Co}(\text{NO}_2)_6^{---}$. The potassium salt of this complex ion is only very slightly soluble and

immediately separates as a fine granular precipitate, yellow by reflected light, but usually almost black by transmitted light.

If precipitated in the cold it separates so finely dispersed as to appear to be amorphous, but from warm dilute solutions tiny cubes and octahedra can be obtained.

This salt can be considered as an analogue of $K_3Fe(CN)_6$. The sodium cobaltinitrite is readily soluble. The corresponding nickel salt is too soluble to separate; hence a separation of cobalt from nickel may be thus accomplished; but the separation is not quantitative.

The test is very sensitive both for cobalt and for potassium (and NH_4 , Rb^+ , Cs^+ , Tl^+) but since characteristic crystals are difficult to obtain it cannot be regarded as a satisfactory identity reaction.

In testing alloys and similar materials this test is of great value, especially since it can be extended to include the "triple nitrite reaction" by following the procedure given on page 186.

If a yellow precipitate is obtained with KNO_2 , indicating the presence of cobalt, decant the supernatant liquid, wash the residue, add one or more drops of concentrated HNO_3 , heat and evaporate to dryness. Test the residue with $K_2Hg(SCN)_4$ as directed in Method A.

When calcium, strontium or barium is present nickel is precipitated with the cobalt (Mayrhofer).

Experiment.

See Lead, Method C, page 184.

C—By Means of Pyridine Hydrochloride and Ammonium Thiocyanate.⁵

Compound Formed — $Co(SCN)_2 \cdot (C_5H_5N \cdot HSCN)_3$.⁶

To the moderately concentrated test drop acidified with HCl add solid (or pasty) pyridine hydrochloride in an amount about

⁵ This is a modification of the test first described by Martini: *Mikrochemie* **7**, 30 (1929). Pyridine, the base, is very volatile, has an intensely disagreeable odor and is moreover irritating and poisonous. These objectionable features are largely eliminated by employing pyridine hydrochloride, without materially affecting the usefulness of the test.

⁶ This formula for the reaction product is suggested by Martini on the basis of the determination of crystallographic constants. The data obtained correspond to those given by Groth for a compound of this formula.

the size of a pin head. Allow to stand a second or two, and if no precipitate has been formed add a large fragment of NH_4SCN .

Examine the preparation with the polarizer in place in order to take full advantage of the extraordinary pleochroism of the colored salts which may be formed. In the discussion which follows it is assumed that the preparation is illuminated with polarized light.

When cobalt is present there is first formed around the thiocyanate fragments a blue zone and often blue oily droplets. In a few seconds long thick angular dendrites made up of rectangular tablets are formed. (See Figs. 126 and 127, page 223. In Fig. 126 the dendrites *R* are due to the reagent and are colorless, the dendrites *B* are a deep blue, whereas those marked *V* are a deep violet.) These crystals appear to belong to the monoclinic system; they exhibit strong pleochroism, the color change being from a light blue to a purple or violet. Pleochroism is best observed in the pinacoidal tablets that always accompany the dendritic aggregates. The rate of separation, habit, color, and hue of the crystals vary greatly with concentration conditions, and there is reason for the belief that the composition of crystals is also variable. It not infrequently happens that, instead of crystals, drops of a blue oil liquid are formed. Under these conditions the preparation should be allowed to stand until the test drop has passed to dryness through spontaneous evaporation. Colored metastable liquids are also formed with a number of different cations and with certain anions, but none of these droplets are blue save when cobalt is present. As the test drop passes to dryness the metastable liquid crystallizes and blue or violet crystals can be readily distinguished in the mass of crystalline residue. The addition of a *very tiny* drop of water dissolves the residue leaving the blue crystals of the cobalt pyridine thiocyanate, thus rendering them clearly visible. In a few seconds these blue crystals disappear and are replaced by blue oily droplets. When the test drop again passes to dryness the blue metastable liquid crystallizes and the typical crystals of cobalt pyridine thiocyanate are formed.

Because of the tendency of the cobalt compound to form metastable oily drops which may not always be readily perceived in the mass of dendritic crystals, it is always best to allow the test drop to pass to dryness and search for blue crystals; these are to be found in segregated masses usually near the circumference of

the drop. Evaporation must not be hastened by heating, for the compound is easily decomposed.

The pyridine-metallo-compounds, formed when the test is performed as above indicated, are all soluble in absolute alcohol and can therefore be readily extracted from the dry residue. Hold the object slide in an almost vertical position with the corner carrying the test drop residue lowest. Allow a small drop of absolute alcohol to flow across the residue and collect at the corner of the slide. A second drop is applied and even a third if necessary. If now the corner of the slide carrying the drops of alcohol is touched to the corner of another clean slide which is also inclined the alcoholic solution will flow onto the clean slide; or the alcohol may be decanted in the usual manner. Holding the slide well inclined during the spontaneous evaporation of the alcohol assures a concentration in a small volume and the deposition of crystals over a relatively small area.

Before performing tests with pyridine and ammonium thiocyanate the analyst should perform a "blank" test by adding to a drop of distilled water a tiny drop of HCl, then a relatively large mass of pyridine hydrochloride, and finally a large fragment of NH_4SCN . Note well the character of the crystals formed by the reagents alone. This "blank" is important since a few cations do not appear to influence the habit of the pyridine salt, while others materially modify it, but not sufficiently to permit identification of the modifying agent.

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , tartrates, oxalates, acetates, arsenates, arsenites, chromates, give no reaction and produce no noteworthy change in the crystals of the reagent.

The chlorides of Ca^{++} , Sr^{++} , Ba^{++} , Mg^{++} , Zn^{++} , Cd^{++} , Hg^{++} , Al^{+++} , In^{+++} , Ti^{+++} , Zr^{+++} , Mn^{++} , Ni^{++} give colorless oily drops or a less dendritic form of the reagent but no crystals which can be used as specific tests.

Since the test is made in a solution acidified with HCl, Ag^+ , Ti^+ , Hg^+ , Pb^{++} , WO_3^{--} (Cu^+ [?]; Au^+ [?]) may be precipitated when the HCl is added.

Fe^{+++} gives a deep blood-red or brownish-colored solution when the thiocyanate is added. If only a small amount of Co^{++} is present and much Fe^{+++} the detection of Co^{++} is impossible, but if the cobalt is in excess of the iron blue crystals can be recognized, especially if the alcohol extraction is employed.

The formation of a precipitate when the pyridine hydrochloride is added to a concentrated solution of chlorides (before the addition of NH_4SCN) indicates the presence of Ti^{+++} , Sn^{++} , Sn^{++++} , Ru^{+++} , Pt^{++++} , Ir^{++++} , Pd^{++++} , or Au^{+++} . But in dilute solutions no precipitate is formed with Ti^{+++} , Sn^{++} , or Sn^{++++} until the NH_4SCN is added; then tablets or radiates of colorless acicular crystals appear at the circumference of the drop.

Rhodium and osmium give only a ring of yellow colloidal matter at the circumference of the drop as it goes to dryness.

Cu^{++} forms two compounds: one, light yellow (Fig. 128, Y, page 223), in large elongated irregular plates or tablets or long somewhat acicular prisms; the other, brown or orange (Fig. 128, B, page 223), in long prisms, singly, in radiates or in irregular masses; these prisms are usually well formed with beveled or pyramidal ends. Both compounds are strongly pleochroic. Sometimes metastable oily drops are formed which do not crystallize until the test drop passes to dryness. Extraction of the residue with absolute alcohol is usually advisable. Copper does not interfere with the detection of cobalt. Uranyl salts and uranates on passing to dryness yield large yellow pleochroic prismatic crystals singly and in radiates. The color and habit are different from those of the light yellow copper compound and there is little danger of mistaking copper for uranium or *vice versa*, especially if the alcohol extraction is practised.

Too much free mineral acid seriously interferes with all tests.

The sensitivity of this pyridine reaction for cobalt, copper, and molybdenum appears to vary greatly according to conditions and is quite low when applied to complicated mixtures.

The reactions given by molybdenum and vanadium have already been discussed on page 222. (See Fig. 125, page 223.)

D-Miscellaneous Tests for Cobalt.

(a)-With HNa_2PO_4 in ammoniacal solution there is formed $(\text{NH}_4)\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$. This salt is isomorphous with the magnesium, nickel, and manganese ammonium phosphates. (See page 121.) It is colorless when seen upon an object slide and therefore indistinguishable from other phosphates which may separate. Decant, leaving the crystalline precipitate attached to the glass; cover the residue with H_2O_2 . If the salt contains cobalt the crystals will turn brown; manganese will behave similarly.

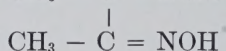
(b)- NH_4OH precipitates a hydrous oxide, readily soluble in excess (separation from iron, etc.). Copper and nickel react similarly.

(c)-If to the strongly ammoniacal solution H_2O_2 is added and the mixture heated to boiling, cobalt is precipitated as Co_2O_3 ; (manganese and nickel are also precipitated).

From mixtures of elements giving precipitates with NH_4OH insoluble in excess, cobalt, copper, and nickel can be separated by digesting the hydrous oxides with strong NH_4OH , centrifuging (or filtering through asbestos) and to the clear solution adding the H_2O_2 . The precipitated hydrous oxides are separated, dissolved in HCl or HNO_3 , and the presence of cobalt confirmed by a suitable test.

DETECTION OF NICKEL

A-By Means of Dimethylglyoxime — $\text{CH}_3 - \text{C} = \text{NOH}$



Compound Formed — $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$.

To a large drop of the solution to be tested add NH_4OH until in slight excess. Warm *gently*. Decant the solution of the hydroxides which have dissolved from those which remain insoluble.

If the ammoniacal solution has too large a volume use only a fraction of it for the test drop.

Prepare a saturated solution of dimethylglyoxime at the corner of a slide. Place near the reagent a drop of the ammoniacal solution obtained as above. Cause the test drop to flow into the reagent. Warm *gently*.

Nickel yields immediately a rose pink or magenta-colored precipitate, so finely divided at first as to appear to be amorphous. On standing a short time, fine acicular pink pleochroic crystals appear either in a felt-like mass or in irregular bristling clusters or in radiates of fine needles (Fig. 130, page 247). Sometimes relatively long very slender tapering prisms are obtained. Often a yellow precipitate is first formed changing slowly into pink or red. The change is hastened by warming.

The pink, magenta, or reddish acicular crystals in alkaline solution are constant and peculiar to nickel; no other element reacts similarly. (See Palladium, page 265).

The test is an exceptionally sensitive one even in the presence



FIG. 130. Nickel with Dimethylglyoxime. 400 $\times$.

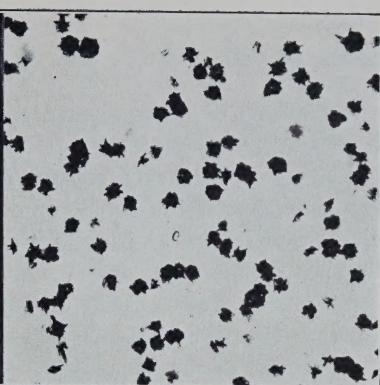


FIG. 131. Ruthenium with Cesium Chloride. 400 $\times$.

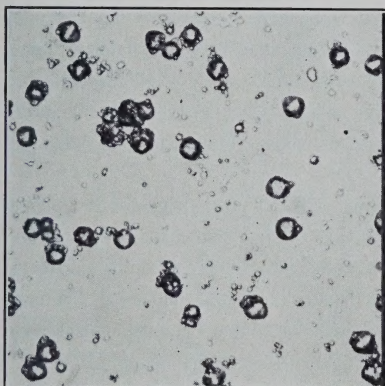


FIG. 132. Rhodium with Potassium Nitrite. 300 $\times$.



FIG. 133. Palladium with Dimethylglyoxime. 150 $\times$.

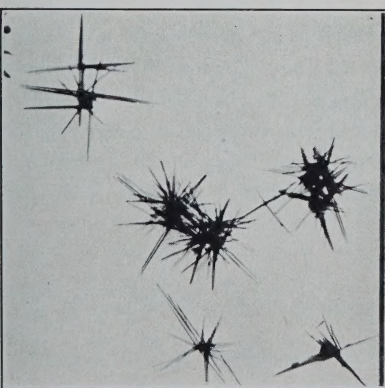


FIG. 134. Palladium with Cesium Chloride. 100 $\times$.

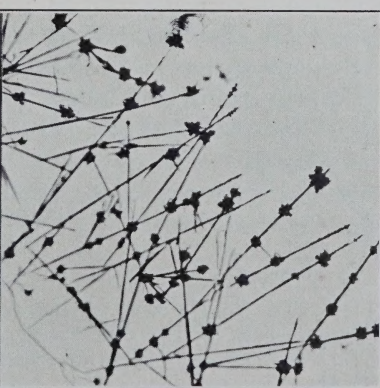


FIG. 135. Palladium with Sodium Iodide and Ammonium Hydroxide 200 $\times$.

of an excess of other elements. Cyanides interfere, due to the formation of a complex ion $[\text{Ni}(\text{CN})_4]^{--}$.

Neither cobalt nor copper give a reaction with dimethylglyoxime, but if the cobalt or copper contains only "traces" of nickel a yellow precipitate is formed that does not readily change to pink on standing or on warming; even under these adverse conditions a careful study of the yellow compound will generally result in the discovery here and there of a few of the characteristic pink needles of the nickel salt. Only when cobalt or copper are in considerable excess do these elements interfere.

Copper can be removed by placing a weakly acidified drop upon a piece of sheet zinc; as soon as a black spot appears, the drop is decanted to a new position. When it is observed that the bright surface of the zinc is not stained at once, the drop is transferred to an object slide, strong NH_4OH is added, and the test for nickel is made as above. If sheet zinc or zinc foil is not available zinc fragments can be used, removing them from the drop as soon as they blacken.

Cobalt can be separated by adding KNO_2 (see page 241) to the acetic acid solution. Decant from the precipitated cobaltinitrite, add NH_4OH to the clear solution and test with dimethylglyoxime.

When a sufficient volume of solution is at hand the interference of cobalt may usually be eliminated by shaking the strongly ammoniacal solution with air, as recommended by Mayrhofer.⁷

Dimethylglyoxime gives with solutions of iron salts a red color. In testing for nickel, therefore, it is usual to obtain an indication of the presence of iron, especially if the material being analysed contains ferrous compounds, for in the presence of ammonium salts the addition of NH_4OH to ferrous solutions will not completely precipitate a hydrous oxide, since double salts such as $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$ or $2 \text{NH}_4\text{Cl} \cdot \text{FeCl}_2$ are formed, and these double salts are relatively stable. If non-volatile organic acids are present NH_4OH will not precipitate a hydrous ferric oxide, and ferric salts will be present in the ammoniacal solution to react with the dimethylglyoxime.

Experiments.

(a) — Try the glyoxime reaction on salts of Ni in NH_4OH and in acid solution, and in different concentrations.

(b) — Try the test upon Co compounds, and mixtures of Ni, Co, Cu and Fe.

⁷ *Mikrochemie d. Arzneimittel u. Gifte* (Berlin, 1923), p. 117.

B—By Means of the Triple Nitrite Reaction.

Compound Formed — $2 \text{KNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{Ni}(\text{NO}_2)_2$.

To the neutral or ammoniacal solution sufficient acetic acid is added to make the test drop distinctly acid. KNO_2 and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ are then added as described under Lead, page 184.

When dealing with mixtures it is more convenient to start with the addition of NaNO_2 and follow some such plan of procedure as is indicated on page 186, bearing in mind the caution given by Mayrhofer⁸ that in the presence of the alkaline earths nickel is precipitated with the cobalt.

If copper is present in excess of nickel the triple nitrite cubes will be colored dark brown or black and will mask the reaction for nickel. Copper can be removed by metallic zinc or iron, provided the reaction is not allowed to proceed too far. It is, however, inadvisable to depend upon the triple nitrite reaction for the identification of nickel, since it is not specific. Always have recourse to Method A.

DETECTION OF COPPER**A—By Means of Potassium Mercuric Thiocyanate— $\text{K}_2\text{Hg}(\text{SCN})_4$.**

Compound Formed — $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2 \cdot \text{H}_2\text{O}$.

The thiocyanate reaction for the detection of copper applies to bivalent copper, but not to monovalent copper compounds. Hence it may first be necessary to treat the material with concentrated HNO_3 , evaporate to dryness, and dissolve the residue in water. The reaction is extraordinarily sensitive when the proper conditions are maintained.

The procedures, precautions to be observed, and sources of error, have been discussed at length under Zinc, page 124.

It is particularly advantageous in the case of copper to make a preliminary test upon a rather highly concentrated test drop, allowing the preparation to stand for several minutes, and after an examination of this preparation, deciding upon the proper dilution which will insure the formation of characteristic crystals.

When the percentage of copper is very low, the addition of a little zinc acetate to the test drop (before the addition of the thiocyanate) will usually render the detection of the copper easier and surer, for the difficultly soluble zinc mercury thiocyanate is

⁸ *Op. cit.*, p. 117.

immediately precipitated and is colored lavender, brown, or even black, by traces of copper too small to be precipitated separately.

Small percentages of copper are generally completely masked by high percentages of cobalt or gold. Nickel may interfere when the test drop consists of a saturated solution of a nickel salt containing a trace of copper only. Dilution eliminates this source of error.

Materials very high in zinc, cadmium, or manganese, and low in copper, yield crystals faintly colored pinkish or lavender; as the per cent of copper increases, the depth of color also increases and finally becomes black, and simultaneously the yellowish green dendrites of the salt $\text{Cu}(\text{SCN})_2 \cdot \text{Hg}(\text{SCN})_2$ begin to appear.

Materials high in Fe^{+++} and low in Cu^{++} yield a double thiocyanate of copper, materially changed in habit and in color and almost masked by the intense red color of ferric thiocyanate. When iron is present, precipitate with NH_4OH , centrifuge or filter, and extract the precipitate repeatedly with strong NH_4OH . Unite the extracts, evaporate to dryness, take up with acid and test with the thiocyanate reagent. In the presence of non-volatile organic acids the iron cannot be removed by this procedure. It is then necessary to ignite just sufficiently to destroy the organic matter, take up with HNO_3 , evaporate to drive off the excess of acid, dissolve in water, and precipitate with NH_4OH .

Another method for the separation of the copper from iron is to place an acidified drop of the solution upon metallic zinc. The copper is precipitated upon the zinc whereas the iron remains in solution. The coating of copper can be scraped off or dissolved off and tested.

If manganese is present add to the ammoniacal solution H_2O_2 and heat to boiling, then proceed as suggested for the removal of iron. This treatment will also remove the cobalt.

In alloys high in lead and low in copper (*e.g.*, anti-friction alloys) the direct detection of copper is often unsatisfactory. It is best to first remove most of the lead by HCl or H_2SO_4 . Alloys very high in silver and low in copper may also give trouble; remove the silver by precipitation with HCl before testing for copper.

Experiments.

See Zinc, Method A, page 124.

(a) — Test for Cu in *very* dilute solution. Repeat, having a small amount of Zn present.

(b) — Prepare a series of tests using varying proportions of Zn and Cu.

B—By Means of the Triple Nitrite Reaction.

Compound Formed — $2 \text{KNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{Cu}(\text{NO}_2)_2$.

This sensitive and characteristic reaction for copper has been described at length under Lead, page 184, Cobalt, page 241, and Nickel, page 249.

Experiments.

- (a) — Test for Cu in CuSO_4 ; in $\text{Cu}(\text{NO}_3)_2$, by the Triple Nitrite Reaction.
- (b) — Try the reaction in acid solution; in ammoniacal solution.
- (c) — Try in like manner a mixture of Cu and Ni, Cu and Co.

C—By Means of Cesium Chloride — CsCl .

Compounds Formed — $2 \text{CsCl} \cdot \text{CuCl}_2$
 $\text{CsCl} \cdot \text{CuCl}_2$.

This reaction is discussed in detail under Tin, pages 77–78; Antimony and Bismuth, pages 204–206 (Fig. 141, page 259).

DETECTION OF SILVER

A—By Means of Hydrochloric Acid — HCl .

Compound Formed — AgCl .

The test drop is strongly acidified with HNO_3 and to it is added the reagent in excess by Method 1 A, page 31.

AgCl is precipitated at once as a heavy curdy mass without recognizable crystal form. The mother liquor is drawn off, the precipitate is washed with water acidified with HNO_3 , and dissolved in NH_4OH . The ammoniacal solution is set aside, and upon spontaneous evaporation and loss of NH_3 tiny cubes and octahedra of AgCl are formed from the decomposition of the compound $\text{AgCl} \cdot 2 \text{NH}_3$ (Isambert). The crystals of AgCl are isotropic and have an extraordinarily high refractive index ($n = 2.07$) and are therefore clearly visible though so small (Fig. 171, page 327).

Thorough washing of the precipitate before dissolving in NH_4OH is essential because there are many compounds that may seriously interfere with the formation of typical crystals; moreover the addition of NH_4OH to an improperly washed precipitate may cause the precipitation of hydrous oxides which may mask the reaction for silver.

AgCl can also be recrystallized by boiling with concentrated HCl , but its solubility in this acid is so low that satisfactory crystals can seldom be obtained. Moreover the fumes arising from

the hot acid are always annoying and may attack the metal parts of the microscope.

TiCl , HgCl , and PbCl_2 are also precipitated by HCl . (See pages 144, 182.)

In materials high in Hg^+ and low in Ag^+ the silver may escape detection because of the reaction of NH_4OH upon the HgCl . It has already been stated (page 144) that this reaction gives $\text{HgCl}\cdot\text{NH}_2$ plus metallic mercury. The finely divided mercury may under favorable conditions reduce the AgCl to metallic silver (Hg is more electropositive than Ag) and thus there may be no AgCl left to be dissolved and recrystallized. On the other hand, Schoorl has shown that under certain conditions recrystallization of AgCl in the presence of HgCl gives rise to a complete change in the crystal habit of the AgCl , and that instead of cubes and octahedra, characteristic highly refractive moss-like dendrites in spherical masses are obtained.

Elements forming oxychlorides under exceptional conditions may be precipitated with the silver.

Precipitation of AgCl must always be made in relatively dilute solutions.

Experiments.

(a) — Precipitate with dilute HCl , a test drop containing AgNO_3 . Separate and wash the precipitate; then crystallize it using NH_4OH as the solvent.

(b) — In like manner test a mixture of AgNO_3 and HgNO_3 .

(c) — Precipitate AgCl , wash, cover with a drop of water, and add a fragment of metallic zinc.

B—By Means of Ammonium Bichromate — $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

Compound Formed — $\text{Ag}_2\text{Cr}_2\text{O}_7$ or Ag_2CrO_4 .

To the test drop add sufficient dilute HNO_3 to make it just distinctly acid. Add a fragment of the reagent to the center of the drop. Allow to stand undisturbed for a few seconds, then carefully transfer to the stage of the microscope.

$\text{Ag}_2\text{Cr}_2\text{O}_7$ (Ag_2CrO_4 (?)) separates in dark red (blood-red or garnet-red) pleochroic plates. Thin plates may appear almost yellow and thick plates practically black. The crystals may be scale-like with irregular outlines, or may be rectangular, or elongated, unsymmetrical, hexagons in outline. Five-sided plates are also formed. The plates occur singly and in irregular aggregates (Fig. 170, page 327).

Insufficiently acidified test drops, or those in which the concentrations are too high, yield tiny rods or slender acicular prisms so dark colored as to appear to be black. On standing such preparations sometimes eventually also yield the more characteristic plates mentioned above.

$\text{Ag}_2\text{Cr}_2\text{O}_7(?)$ can be recrystallized from hot water but this procedure gives poor results. Far better preparations can be obtained by recrystallizing from hot $\text{HNO}_3(1 : 4)$.

Silver bichromate is readily soluble in NH_4OH . On standing dark red acicular crystals, skeletal forms, and dendrites separate. These crystals are believed to be complex salts containing one or more molecules of NH_3 , probably $\text{Ag}_2\text{CrO}_4 \cdot 4 \text{NH}_3$.

The test drop should always be acidulated with HNO_3 , otherwise chromates of a number of other elements may be precipitated. (See pages 115, 149, 233.) When recrystallizing from NH_4OH the possible interference of these elements must be taken into account.

Normal orthorhombic K_2CrO_4 added to neutral solutions of AgNO_3 causes a precipitation of normal Ag_2CrO_4 , but when the test drop is first acidified with HNO_3 the crystals separating may be either Ag_2CrO_4 or $\text{Ag}_2\text{Cr}_2\text{O}_7$, or a mixture, depending upon conditions of concentration and of acidity and upon the presence or absence of other ions. When recrystallized from hot HNO_3 the salt separating usually consists of $\text{Ag}_2\text{Cr}_2\text{O}_7$ alone.

In cold solutions lead is precipitated as heavy, bright yellow, pulverulent PbCrO_4 without recognizable crystal form, but from hot solutions, thin, long, slender monoclinic prisms are obtainable. This salt is soluble in solutions of NaOH or KOH . If, however, only a minute quantity of alkali is brought into contact with the lead chromate a bright red basic chromate is formed.

When much lead is present the bichromate reaction for the detection of silver may fail, for instead of the dark red plates, small yellow prisms separate. In such an event first remove most of the lead with dilute H_2SO_4 , using a very dilute test drop. The test drop must be dilute with respect to silver, for otherwise Ag_2SO_4 may be precipitated. When H_2SO_4 is present, crystals of Ag_2SO_4 separate with Ag_2CrO_4 and $\text{Ag}_2\text{Cr}_2\text{O}_7$. The crystals of Ag_2SO_4 are, however, not colorless but are pleochroic and yellow or brownish-red because of a solid solution of Ag_2CrO_4 in Ag_2SO_4 . Normal orthorhombic Ag_2CrO_4 is isomorphous with Ag_2SO_4 , Ag_2SeO_4 , and anhydrous Na_2SO_4 .

Mercurous salts in HNO_3 solution give a number of different compounds (See Mercury, page 149; Fig. 90, page 137), depending upon the conditions under which the test is made. These compounds differ sufficiently in habit from $\text{Ag}_2\text{Cr}_2\text{O}_7$ to prevent confusing Hg^+ and Ag^+ , but if much Hg^+ is present the dark red crosses and irregular bundles of prisms may completely mask the $\text{Ag}_2\text{Cr}_2\text{O}_7$ crystals when the silver is present in very small amount only. Mercurous chromate is insoluble in alkalis, a distinction from lead. Bismuth salts yield irregular dendritic masses, small prisms, and hexagonal grains, which are orange or reddish brown in color. The compound is probably bismuthyl bichromate $(\text{BiO})_2\text{Cr}_2\text{O}_7$.(?)

Dark red silver salts resembling the chromates are formed by arsenates. Vanadates form yellow or orange silver salts.

White alloys believed to contain silver can be tested for this element by drawing across a smooth surface a streak of a solution of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in HNO_3 . The color of the streak (in the absence of bismuth) is generally sufficient to indicate the presence or absence of silver. But if the streak is examined under the microscope by reflected light there can be no doubt as to the presence or absence of silver, for the characteristic crystals of $\text{Ag}_2\text{Cr}_2\text{O}_7$ can be readily perceived.

Experiment.

See under Chromium, Method A, page 216.

C-By Means of Ortho-arsenic Acid or Ortho-arsenates — H_3AsO_4 .

Compound Formed — Ag_3AsO_4 .

The reagent is applied by Method I, page 30, to the neutral or very slightly acid (HNO_3) test drop.

The best results are obtained when part of the H_3AsO_4 in the reagent has been neutralized with NH_4OH but care must be observed that the acid *is never completely neutralized*.

Silver ortho-arsenate separates first as a fine, reddish, granular precipitate, rapidly changing to reddish brown with a tinge of violet, or changing into black crystallites, plates, and prisms of the hexagonal system. Incompletely developed hexagonal plates are also formed. One of the characteristic features of this salt is the great variety of peculiar forms assumed by its crystals (Figs. 156, 157, page 311). Well-formed, well-developed crystals

are seldom seen; the typical crystals are irregular dendrites, but aggregates bristling with fine parallel needles may develop on standing or on recrystallization from NH_4OH .

Ag_3AsO_4 is insoluble in acetic acid, moderately soluble in hot HNO_3 , and readily soluble in NH_4OH . Recrystallization from NH_4OH gives characteristic crystals. In the absence of air the ammoniacal solution deposits colorless needles of the compound $\text{Ag}_3\text{AsO}_4 \cdot 4 \text{NH}_3$ (Widman). This tetra-ammonia salt turns red when it comes in contact with the oxygen of the air, or when it loses NH_3 .

Although the color and habit of Ag_3AsO_4 are sufficiently characteristic to permit the easy recognition of silver in simple mixtures, the test cannot be considered as a dependable one since most of the metals usually associated with silver are also precipitated by orthoarsenic acid and may seriously interfere with or mask the reaction.

Experiments.

(a) — Test a neutral solution of AgNO_3 with H_3AsO_4 , in the manner suggested above.

(b) — Recrystallize a preparation of Ag_3AsO_4 from HNO_3 .

(c) — Try recrystallizing another preparation with NH_4OH . Allow to stand after reprecipitation, and examine.

(d) — Test a mixture of Ag and Pb; then one of Ag and Hg.

DETECTION OF THE PLATINUM GROUP

Ru, Rh, Pd; Os, Ir, Pt; Au

The rare elements of Group VIII, known also as the platinum metals, consist of gold (of Group I) and the two triad groups, ruthenium, rhodium, and palladium, and osmium, iridium, and platinum. In microscopical qualitative analyses of materials containing these elements the analyst finds himself confronted by almost insuperable difficulties. These difficulties are not so much a question of doubtful identity tests as of unsatisfactory separation methods when dealing with very small amounts of material. Moreover, these elements are not readily brought into solution.

Although the platinum metals are always found associated, can be separated only through complicated reactions, and have many properties in common, paradoxically, in no other triad groups do we find such widely divergent chemical properties.

Fortunately it is seldom that the analyst is required to make an analysis of material of absolutely unknown composition. The problem is usually to determine which of the platinum group are present in ores or alloys, or in salts. The salts, however, are seldom combinations of simple ions but are usually compounds in which the platinum metals are so combined with other elements as to form complex ions. In these complex ions the elements there combined seldom respond to their specific tests. Either the complex must first be destroyed or the analyst must be familiar with the chemical behavior of the rare metal complex ions which are likely to be encountered.

In the discussions of the tests as given in the following pages the authors assume that the material has finally been brought into solution by evaporation with aqua regia or through the action of chlorine gas, and that the excess of acid or chlorine has been removed. This treatment will give ruthenium, rhodium, and palladium as chlorides; iridium as chloroiridic acid; platinum as chloroplatinic acid; and gold as chloroauric acid. Osmium will probably have been driven off as the very volatile OsO_4 or as chlorine compounds. Osmium therefore does not usually enter into the tests described for the other platinum metals, but must be sought by wholly different procedures; osmium may, however, remain in the aqua regia solution if the heating has not been at too high a temperature.

DETECTION OF RUTHENIUM

A—By Means of Cesium Chloride — CsCl .

Compound Formed — $2 \text{CsCl} \cdot \text{RuCl}_3(?)$.

To the dilute test drop containing RuCl_3 , acidified with HCl , the reagent is added by Method I or Method II.

A double chloride of cesium and ruthenium, of uncertain composition, is first precipitated as a barely visible turbidity; later exceedingly minute highly refractive spherical grains appear; these appear black by transmitted light but are faintly yellowish or brownish by reflected light. After standing some minutes tiny dark brown disks are formed, many of them having a distinctly hexagonal outline; those near the circumference of the test drop gradually become drusy and finally develop into tiny bristling

radiates (Fig. 131, page 247). The sequence — tiny grains, disks, and radiates — appears to be specific for ruthenium.

Rhodium tested in the same way in dilute solution yields a precipitate whose refractive index is so near that of the solution that no details of structure can be resolved, but as the drop passes to dryness, anisotropic, cylindrical, oval, and lenticular crystals of a reddish-brown color appear; imperfectly developed prisms are also formed. Rhodium does not appear to interfere with the detection of ruthenium.

Palladium forms light brown, long, very slender acicular crystals, with ends tapering to a point, and are thus typical needles. The great majority of the crystals grow singly from the circumference into the drop. These needles also form curious irregular radiates that are specific for palladium (Fig. 134, page 247). Another characteristic feature of these radiates is the formation of queer, irregular, thin plates projecting from one side. The palladium salt is strongly birefringent and exhibits brilliant polarization colors. The extinction appears to be very slightly oblique. As the concentration rises, from spontaneous evaporation, irregular aggregates of short, stout, tapering prisms are to be found.

Mixtures of ruthenium and palladium tested by Method II usually give at once, near the reagent fragment, masses of almost colorless typical trichites in long curving plume-like tufts, often extending completely across the field of the microscope. The individual filaments are so fine as to appear black. Near the circumference of the test drop disks of $2 \text{ CsCl} \cdot \text{RuCl}_3(?)$ can be found, and later atypical needles of the palladium double salt appear. If a tiny drop of water is brought in contact with the trichiten crystals, they disappear at once and are replaced by the tapering acicular crystals of the palladium salt.

With platinum the same type forms as of K_2PtCl_6 are obtained, but always very much smaller. (See Potassium, page 66.)

In very dilute solutions containing iridium no separation of crystals occurs, and no indication of the salt Cs_2IrCl_6 is obtained until evaporation has taken place. Concentrated solutions of iridium (IrCl_6)— yield yellow rough spherical grains, irregular disks, rosettes and lenticular crystals, singly or in aggregates. Under very favorable conditions octahedral crystals are obtained. The salt Cs_2IrCl_6 is isomorphous with K_2PtCl_6 . With rubidium

chloride similar but larger crystals are formed (Fig. 147, page 269).

Both iridium and platinum unite with NO_2^- to form stable complex ions, the alkali salts of which are soluble.

B-By Means of Thiourea — $\text{SC}(\text{NH}_2)_2$.

Compound Formed — Blue Color.⁹ (Composition unknown.)

Place near the corner of an object slide a large drop of concentrated HCl . To this drop add sufficient of the solution to be tested to impart to it no more than a yellowish or brownish tint. It is important that the test drop shall be dilute with respect to the concentration of the chlorides of the platinum metals.

Add to the test drop several fragments of thiourea, a volume not less than this (o). Allow to stand for a short time; examine under the microscope. If crystals appear note their habit. Warm the preparation and then hold it over a pure white background.

Ruthenium gives a beautiful clear blue color. The reaction is very sensitive and appears to be specific for ruthenium.

If the solution is too concentrated the color produced is a greenish blue and so intense as to be almost black (the green being the result of the yellow of the RuCl_3 plus the blue of the compound formed by the thiourea).

Warming is essential for the development of the color, although at times, on standing at room temperature, a recognizable blue tint may appear.

Osmium as OsO_4 in concentrated HCl gives instantly in the cold a deep carmine-red color and red crystals are formed. According to Tschugaeff¹⁰ the red color is due to the formation of a complex having the formula $\text{Os}(\text{NH}_2 \cdot \text{CS} \cdot \text{NH}_2)_6 \cdot \text{Cl}_3 \cdot \text{H}_2\text{O}$. These crystals usually take the shape of thin rectangular plates, of H's, X's, or may be envelope-like in appearance. The crystals are pleochroic, strongly birefringent and exhibit high order polarization colors. The envelope-like crystals may grow into aggregates of thin irregular plates. Irregular radiates are commonly present (Fig. 138, page 259).

In addition to the skeletal crystals there appear to be always formed many tiny crystalline aggregates that develop into thick

⁹ Wöhler and Metz: *Zeit. anorg. Chem.* **138**, 368 (1924).

¹⁰ *Compt. rend.* **167**, 235 (1918).

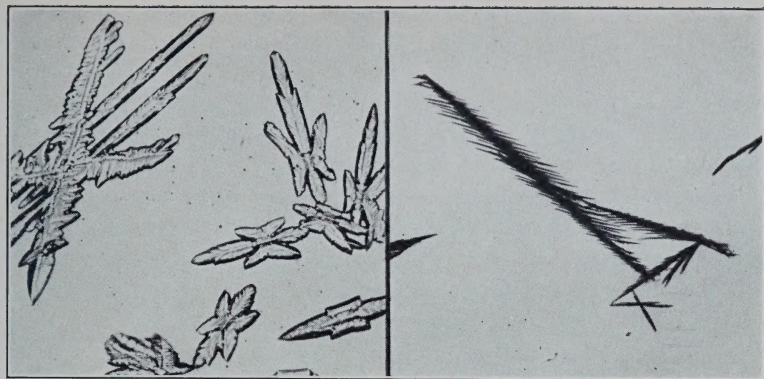


FIG. 136. Palladium with Thiourea.
100 $\times$.

FIG. 137. Platinum with Thiourea.
100 $\times$.

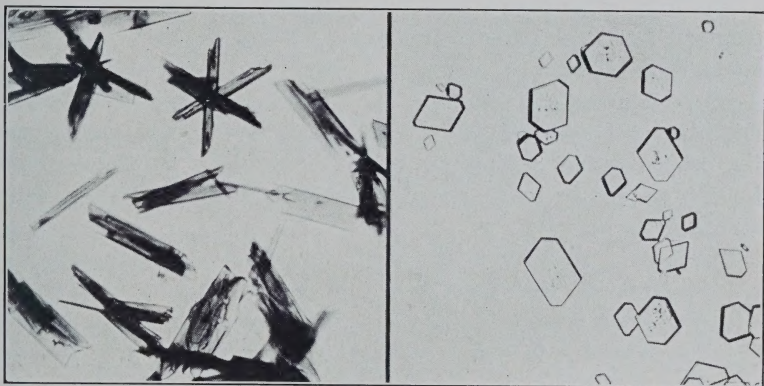


FIG. 138. Osmium with Thiourea.
100 $\times$.

FIG. 139. Gold with Thiourea.
100 $\times$.



FIG. 140. Gold with Thallous
Nitrate. 70 $\times$.

FIG. 141. Copper with Cesium
Chloride. 100 $\times$.

stars, so deeply colored as to appear black. This compound is probably anisotropic, but the crystals are too thick and too deeply colored to permit accurate observations.

Preparations containing both ruthenium and osmium, when warmed, give varying shades of violet or purple according to the relative amounts of these two elements, *i.e.*, depending upon whether blue or red predominates. In mixtures the separation of the osmium crystals is retarded but not prevented. In mixtures of ruthenium and osmium, the crystals of the osmium compound are smaller and their tint slightly changed, but in all proportions both ruthenium and osmium can be detected simultaneously.

Rhodium gives first a very finely granular precipitate growing outward from the reagent fragment. When heated there is no appreciable change in color, but curious small reddish-brown botryoidal masses appear and the granular precipitate becomes flocculent. These peculiar crystal masses are formed only when the concentration of rhodium is relatively high. In dilute solutions none are to be found until the test drop has passed substantially to dryness.

Mixtures of ruthenium and rhodium give the blue reaction for ruthenium unless the concentration of rhodium is very high, when a tinge of green is alone obtainable. But if the caution given above is followed and a test drop employed which is only just faintly yellow, an unequivocal reaction for ruthenium can always be obtained. When both ruthenium and rhodium are present in considerable amounts, there usually appear, after heating, deep blue-black disks, spheres, and botryoidal masses.

Test drops containing H_2IrCl_6 are decolorized when thiourea is added. The decolorization proceeds more rapidly on warming. The original reddish solution eventually becomes water-white. No crystals separate. The presence of iridium appears to have little effect upon the color reaction for ruthenium. The only influence exerted appears to be a slight lowering of the sensitivity of the reaction, *i.e.*, the intensity of the blue is reduced but its hue is unchanged.

Palladium gives instantly, in the cold, a yellow or orange zone about the reagent fragments. Under the microscope the outer edge of the advancing zone is seen to consist of small orange-red or brown moss-like dendritic aggregates. In concentrated solu-

tions this orange-red, finely crystalline, difficultly soluble compound coats the reagent fragments and prevents the reagent from passing into solution.

Between the zone in which this difficultly soluble orange compound exists and the reagent fragments, a second very characteristic bright yellow compound is formed. It separates in skeletal crystals in the shape of halberd heads (Fig. 136, page 259), rhomb-shaped plates or rhombs in which both acute angles are cut off perpendicular to the long axis of the rhombs. Radiates of slender prisms are also formed. All crystals are strongly birefringent, show brilliant polarization colors, and the prisms and plates give oblique extinction. The habit of the crystals formed with thiourea varies with concentrations of reagent and palladium.

Mixtures of palladium and ruthenium, when warmed, give the clear blue of ruthenium without destruction of the palladium crystals. But if ruthenium is greatly in excess of palladium, the halberd type of crystal is replaced by X's and short stout prisms.

Platinum (as H_2PtCl_6) like palladium gives in the cold two different compounds, one yellow, one brown; usually the former exists for only a short period and is replaced by an abundance of long reddish-brown feathery dendrites (Fig. 137, page 259).

Mixtures of ruthenium and platinum, warmed, give the blue of ruthenium. In the cold the formation of typical crystals of platinum is not prevented. Heating dissolves them and they reappear on cooling.

Gold gives an orange-red precipitate in the cold, with a slight reduction to metallic gold, but in the zone immediately about the reagent, thin, practically colorless, hexagonal plates singly and in foliated masses are formed. They are weakly birefringent and exhibit blue and gray polarization colors. Heated they dissolve and reappear on cooling (Fig. 139, page 259).

Mixtures of ruthenium and gold give the blue color of ruthenium and the orange-red and colorless crystals of the gold compounds.

Many bivalent elements give a white granular or exceedingly fine crystalline precipitate with thiourea in the cold, but in all the cases we have tried there has been no prevention of the blue color of ruthenium, nor does there appear to be interference with the formation of the crystalline precipitates given by the platinum group of metals.

Cobalt salts give a blue color *at once, in the cold*, when added to

concentrated HCl before the thiourea is added, the latter reagent causes no change.

Thiourea appears to be one of the most useful reagents for differentiating between the members of the platinum group, for not only does it give characteristic crystalline precipitates or a color with each of them, but curiously enough, it is serviceable in mixtures if such mixtures are not too complex.

In the case of palladium, osmium and platinum two different compounds appear to be formed, one in the zone where there is present an excess of the salt of the element, the other in the zone close to the reagent fragment where the solution contains an excess of the reagent. Although this complicates matters by introducing a large number of variables it does not render the reactions impossible of interpretation, for the modified crystals formed are almost without exception characteristic of the mixtures.

The analyst will have little difficulty in interpreting the reactions obtained, if he will always use large fragments of the reagent, test drops at least twice as large as customary in other tests, and *never neglect to perform the test on several different concentrations* of the material in concentrated HCl. It is also essential that the preparations be allowed to stand for some time at room temperature.

The following tabulation may serve as a guide in the interpretation of results, but it is obvious that it does not, and cannot, include all the combinations possible.

The preparation is allowed to stand at room temperature for a short time and then examined under the microscope:

Red H's, X's, prismatic plates	Os
Thick brownish-red or black stars and aggregates	Os
Brown, reddish-brown or black botryoidal grains	Rh
Brown dendrites, usually feathery	Pt
Dark colored (brown?) moss-like groups of very tiny crystals	Pd
Yellow skeleton crystals, rhombs, elongated six-sided plates	Pd
Orange-red tiny dendrites	Au, Os
Colorless hexagonal plates in foliated masses	Au
Yellow radiates of acicular prisms and brown feathery dendrites	Pd and Pt
Brownish moss-like aggregates and brown feathery dendrites	Pd and Pt
Very large radiating groups of feathery dendrites, either colorless or rose pink (pleochroic)	Os and Pt

After warming, the preparation is held over a white background:

A clear blue color.....	Ru, (Co)
A red color and crystals.....	Os
A violet or purple color.....	Ru and Os

DETECTION OF RHODIUM

A-By Means of Potassium Nitrite — KNO_2 .

Compound Formed — $3 \text{KNO}_2 \cdot \text{Rh}(\text{NO}_2)_3$.

The reagent is applied by Method II, page 32, to a dilute test drop acidified with acetic acid.

In a few seconds a faintly yellow turbidity results, which slowly increases in amount, becomes distinctly granular in character and finally develops into tiny rough rounded grains, singly, in strings of two or three, or grouped in irregular botryoidal masses (Fig. 132, page 247). These crystalline grains are isotropic. For their resolution a magnification of 150 to $200\times$ is usually essential.

When formed very slowly from dilute solutions, cubical and octahedral grains can be found, but these always have their edges and angles rounded.

If the test drop is highly concentrated with respect to rhodium, there will be formed about the fragment of KNO_2 a reddish-brown zone, of a turbidity so dense that its resolution into distinct crystalline granules is impossible.

The addition of CsCl increases the sensitivity of the test to a certain degree, but little appears to be gained as regards the size of the crystals or the character of their development. In many cases the addition of CsCl is undesirable because of its marked tendency to form easily crystallizable double chlorides with other elements, and the separation of these double chlorides may completely mask the reaction for rhodium.

The nitrite reaction permits the detection of rhodium in the presence of ruthenium and palladium.

In dilute solutions ruthenium yields no precipitate, or at the most only a very slight turbidity of what appear to be tiny black grains which neither increase in numbers nor in size on standing. In very concentrated solutions a faint brown flocculent precipitate may be produced or tiny colorless(?) isotropic disks may appear, but these cannot be confused with the rhodium salt.

Palladium is not precipitated, but just before the drop passes

to dryness through spontaneous evaporation there separate near the circumference of the drop long, narrow, irregularly tapering, bent prisms of a bright yellow color. Masses of trichiten crystals are also obtained, but no globulites.

In solutions containing H_2IrCl_6 or H_2PtCl_6 a precipitate of K_2IrCl_6 or K_2PtCl_6 is obtained, or if the conditions are just right, a complex soluble iridonitrite or platinonitrite may be formed.

Osmium gives no perceptible reaction with KNO_3 .

Cobalt forms a yellow difficultly soluble double nitrite that is indistinguishable from that of rhodium. (See Cobalt, page 241.)

If lead is present nickel and copper will be precipitated also. (See Triple Nitrite Reaction, page 184.)

B-By Means of Thiourea. — See pages 258-263.

DETECTION OF PALLADIUM

A-By Means of Sodium Iodide — NaI.

Compounds Formed — PdI_2

$\text{PdI}_2 \cdot 2\text{NH}_3$.

To a moderately dilute solution add the reagent by Method II.

The fragment of NaI is immediately covered with a dense, opaque black precipitate appearing somewhat granular in a zone about the black-coated reagent fragment, and the liquid immediately in contact with the reagent turns brown due to the formation of a soluble double iodide; PdI_2 is slightly soluble in excess of the reagent.

Apply a drop of NH_4OH (1 : 1) by Method I. There are formed almost at once very long slender hair-like dark brown crystals appearing jet black. These long straight hairs form a network resembling an irregular spider-web. Shortly after the separation of the slender prisms, tiny irregular bristling aggregates are formed, free and attached at intervals along the hairs like a string of rough beads. These tiny aggregates develop into crosses, stars, and lichen-like radiates, or into radiates of fine needles; there can be seen also curious acicular dendritic clumps (Fig. 135, page 247).

A test giving such a great variety of crystal forms is always unsatisfactory, since it is next to impossible to control conditions so as to obtain the particular type of crystal that is strictly characteristic of the ion sought. However, the very long, very slender,

opaque crystals that first separate appear to be specific for palladium.

From somewhat concentrated solutions, with an amount of NaI insufficient to convert all the palladium into PdI_2 , there will be formed around the circumference of the test drop brownish-yellow straight and curving dendrites of the compound $\text{PdCl}_2 \cdot 2\text{NH}_3$.

Ruthenium in dilute solutions gives no crystal formation, but in concentrated test drops there is produced a black cloud, and when NH_4OH is added there is an instantaneous formation of an opaque black mass.

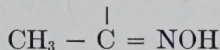
Rhodium forms first a dark orange precipitate about the NaI fragments; then there appear in a zone about these fragments deep yellow or orange disks. These disks in turn disappear and are replaced by a few tiny deep orange grains. The addition of NH_4OH produces an immediate precipitation of an orange-colored gel.

With H_2PtCl_6 and H_2IrCl_6 , NaI gives no crystals other than the separation of iodine as a dense black precipitate, which may be crystalline or granular according to concentrations, acidity, rate of decomposition of NaI, etc. If NH_4OH is added there will be formed the yellow octahedra of $(\text{NH}_4)_2\text{PtCl}_6$, the red octahedra of $(\text{NH}_4)_2\text{PtI}_6$, and mixtures of the two. With iridium the corresponding deeply colored $(\text{NH}_4)_2\text{IrCl}_6$ and $(\text{NH}_4)_2\text{IrI}_6$ will be obtained.

KI may be substituted for NaI with advantage except when platinum or iridium are present.

For the behavior of other elements with KI, see pages 146-148.

B-By Means of Dimethylglyoxime — $\text{CH}_3 - \text{C} = \text{NOH}$



Compound Formed — $\text{Pd}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$.

The aqua regia solution of the material to be tested is evaporated to dryness to remove the excess of acids; to the residue one or two drops of water are added, and then a large drop (about half the size of the test drop) of concentrated HCl. Several small fragments of dimethylglyoxime are then fully submerged in the test drop, and the preparation set aside for a few minutes.

If palladium is present the glyoxime fragments become covered with short, projecting, slender yellow needles which appear [to be brown or black under the microscope. These needles attain

a considerable length, a few become detached from the reagent and form radiates or irregular aggregates, but the majority remain attached to the reagent fragments (Fig. 133, page 247).

When the test drop is of sufficient size to insure standing for some time without evaporating to dryness, yellowish-brown, delicate, long, thin prisms with square ends are formed. These prisms usually occur singly, near the reagent, but not attached thereto; they are of unequal width throughout their length and can be seen to be crossed by many parallel lines at right angles to their length; examined between crossed nicols this peculiar structure is shown to be due to twinning.¹¹ These prismatic crystals exhibit brilliant polarization colors and extinguish parallel to their direction of elongation.

This reaction, especially the peculiar and characteristic twinning, appears to be specific for palladium, but it is essential that the reagent be added to a test drop strongly acidified with HCl.

According to Putnam, Roberts, and Selchow, who have made a comprehensive study of this test for palladium, there are no other elements that give a similar reaction under the conditions outlined, nor are there any interferences with the test under these conditions.

The addition of the reagent by Method I has not proved satisfactory in our hands; an immediate precipitate of short, very fine, lemon-yellow needles is produced in a thin cloud. Even on long standing these tiny crystals rarely develop into forms of such size and character as to constitute a reliable test.

It is sometimes stated that platinum and gold react with dimethylglyoxime. We have been unable to confirm this in the case of platinum as H_2PtCl_6 , but with gold as HAuCl_4 , on long standing, tiny very faintly yellow prismatic plates with oblique ends are obtained. These plates are strongly birefringent and exhibit oblique extinction, but do not develop into the long twinned crystals characteristic of the palladium compound.

C—By Means of Thiourea — $\text{SC}(\text{NH}_2)_2$. — (See pages 258–263.)

D—By Means of Ammonium Thiocyanate and Thallous Nitrate.
Compound Formed — $2 \text{TlSCN} \cdot \text{Pd}(\text{SCN})_2(?)$.

To the large test drop, which must be moderately concentrated with respect to palladium, add fragments of NH_4SCN , stirring

¹¹ Putnam, Roberts, and Selchow: *op. cit.*, p. 430.

until any brown precipitate at first produced has completely dissolved. Drop into the preparation several small crystals of TiNO_3 . Heat to boiling. Allow to cool slowly; do not chill on metal.

A yellowish-brown crystalline precipitate results, growing into lenticular prisms usually united in threes or in more or less symmetrical crosses or in irregular radiating aggregates. These crystals are remarkable for their light-scattering powers and appear to be jet black by transmitted light.

If the preparation is chilled great numbers of curious tiny dendritic aggregates are obtained in forms resembling lichens or clumps of moss.

To solutions of ruthenium chloride the addition of NH_4SCN changes the yellow liquid first to brown, then to plum color or a reddish purple. After the addition of TiNO_3 and boiling, a violet solution is obtained, from which separate violet or black, rough, three-armed or four-armed dendrites; later long, doubly tapering needles appear, singly and in loose radiates of few arms. These needles are difficultly soluble in hot water, are strongly birefringent and show brilliant polarization colors, with an extinction very slightly oblique. The dendritic aggregates are, however, readily soluble in hot water, from which they separate on cooling so black that only their angular outlines can be made out.

Rhodium gives a brown amorphous precipitate, insoluble in boiling water and showing no evidence of crystallization.

Platinum and iridium give minute isotropic octahedra.

This interesting reaction is of value as a confirmatory test only and is not applicable to routine qualitative analyses, especially when dealing with complex mixtures.

E—Other Tests for Palladium.

(a)—With KCl added by Method II to an aqua regia solution there are obtained long slender yellow prisms with oblique ends. These prisms are strongly birefringent and exhibit brilliant polarization colors. Some give an extinction very slightly oblique to their direction of elongation; others appear to have parallel extinction. In solutions which are very strongly acid no crystals are at first formed, and the prisms appear after long standing only.

(b) With TiNO_3 there is an instantaneous formation of a light brown granular precipitate unless the solution is very dilute.

If sufficiently dilute, curious black dendritic radiates are formed with arms ending in disks; crosses and X's also abound. The latter appear to be skeletons of rectangular plates.

(c)–With NH_4OH added by Method I to test drops strongly acidified with HCl , long, slender, rose-pink needles are formed in a felted mass. After standing a few minutes one end of these needles begins to sprout and soon great feathery tassels are formed. If the solution is sufficiently concentrated with respect to palladium some of the needles eventually broaden and become long, sharp-pointed prisms, which are strongly birefringent and show brilliant polarization colors. Their extinction is oblique, somewhat less than 10° . Ruthenium gives a black granular or flocculent precipitate, but no crystals. Rhodium gives a precipitate, similar, but reddish brown in color.

(d)–With oxalic acid and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. See Calcium, page 106.

(e)–With aniline hydrochloride in dilute test drops acidulated with HCl , curious polysynthetic prisms built up of thin plates, skeletal crystals, rhombs, and irregular tablets are obtained. These plates and prisms have oblique ends, are strongly birefringent and strongly dichroic, passing from lemon yellow to brown. Their extinction is oblique and they exhibit brilliant polarization colors. Twins are commonly formed. The appearance of the crystals is highly characteristic of palladium (Fig. 142, page 269).

Platinum gives very faintly yellow thin irregular plates and dendritic masses, wholly different in appearance from those formed by palladium and of an entirely different color (Fig. 143, page 269).

Iridium forms greenish X's and irregular skeletal and dendritic crystals, in appearance recalling PbCl_2 when precipitated in the cold by HCl . There is also formed a greenish-blue, amorphous precipitate resulting from the oxidation of the aniline (Figs. 144, 145, page 269).

Rhodium gives a yellow amorphous precipitate, and when the preparation passes to dryness a few small sheaves, radiates, and aggregates of dendritic crystals sometimes appear.

Ruthenium fails to react under the conditions of the test.

Osmium gives a colorless, crystalline crust around the circumference of the drop. No definite crystals are formed and no positive reaction is obtained.

Gold yields no crystals, but the aniline is oxidized by the HAuCl_4 and a dense flocculent dark green precipitate results.

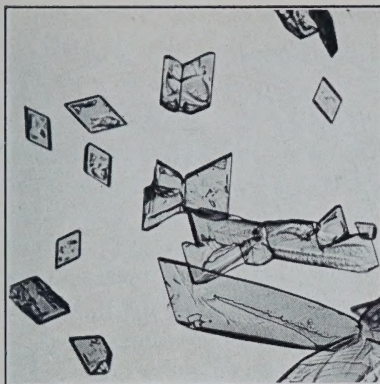


FIG. 142. Palladium with Aniline Hydrochloride. 100 $\times$.

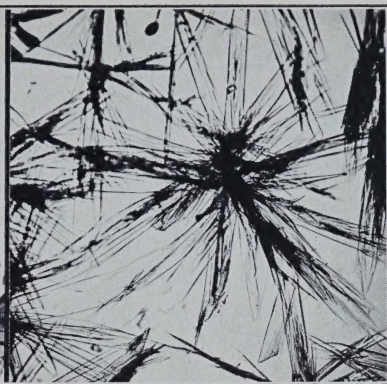


FIG. 143. Platinum with Aniline Hydrochloride. 50 $\times$.

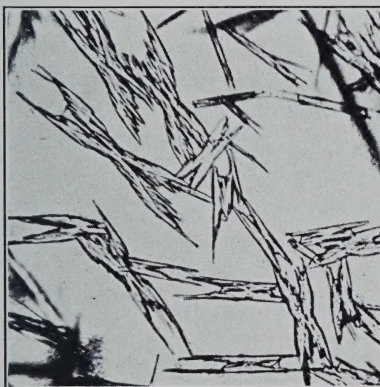


FIG. 144. Iridium with Aniline Hydrochloride. 200 $\times$.

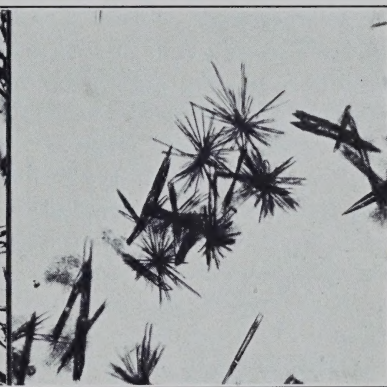


FIG. 145. Iridium with Aniline Hydrochloride. 70 $\times$.



FIG. 146. Platinum Precipitated as Cupric Platinotetrammine Hydrochloride. 100 $\times$.

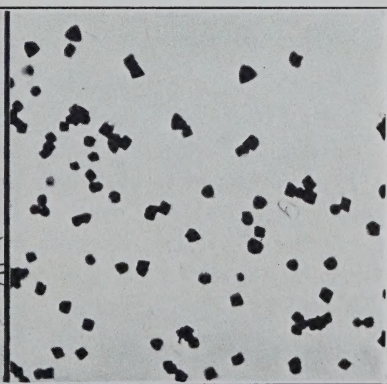


FIG. 147. Iridium with Rubidium Chloride. 200 $\times$.

DETECTION OF OSMIUM

The microscopic detection of osmium is difficult and unsatisfactory save when dealing with a comparatively pure product such as "osmic acid" — OsO_4 . The chief difficulty lies in the extraordinary volatility of the oxides and chlorides. If the material under examination is treated in the usual manner it is probable that all of the osmium will be lost through volatilization, unless iridium is also present and the alloy "Osmiridium" is formed or present. It is therefore imperative that the attack by aqua regia shall be made in a distilling tube¹² of the types illustrated on page 16. The receiving end should be kept cool and should contain a strong solution of KOH. Behrens' suggestion that the condensate from the attack with aqua regia be received in a well-cooled tube and subsequently fractionated into KOH is a wise one, and the slightly increased time and labor involved are offset by the increased certainty of results.

Residues insoluble in aqua regia can be fused with KOH and KClO_3 (1 : 1) in a tiny porcelain crucible and maintained at a low red heat until decomposition is complete. When thoroughly cool, the fused mass is moistened with water, a few drops of concentrated HNO_3 added, and the crucible covered immediately with an object slide carrying a hanging drop of strong KOH (Behrens).

HNO_3 converts osmium into volatile OsO_4 . Although osmium forms both OsCl_2 and OsCl_4 , the tetroxide OsO_4 is the most stable compound of osmium, but even the osmates of potassium or sodium are relatively unstable, though their solutions permit of being concentrated at a gentle heat without loss of osmium.

Osmium is tested for by the addition of alcohol as below.

A—By Means of Potassium Hydroxide and Alcohol.

Compound Formed — $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$.

If the material to be tested is a water-soluble crystalline compound, dissolve it in a drop of a strong solution of KOH placed at the corner of a slide. Osmium will give in KOH a yellow or brown solution. Test the reaction by touching the drop with a "litmus-silk" fiber. The drop must be strongly alkaline.

Tip the slide at an angle of about 30° so that the test drop is at

¹² See also Behrens-Kley, op. cit. p. 250.

the lowest point, add a tiny drop of absolute alcohol about 2 mm. above the test drop, and allow it to flow into the test drop. If the slide is not tipped the alcohol and test drop mixing will flow over the slide. In a few seconds add another drop of alcohol. As soon as all action has ceased examine the preparation under the microscope, first holding it over a white background to observe the color.

Potassium osmate, $K_2OsO_4 \cdot 2 H_2O$, separates in well-developed, clear-cut, violet, highly refractive orthorhombic "octahedra" which are strongly birefringent and exhibit brilliant polarization colors. Many of the octahedra show pinacoidal faces, and many develop into elongated forms. This salt is readily soluble in hot water and can be recrystallized repeatedly. Occasional preparations are obtained in which all the crystals first formed are elongated pseudo-octahedra (Figs. 148, 149).

When the material to be tested consists of a condensate which has been absorbed in KOH, a drop is placed at the corner of a slide and the alcohol applied as above.

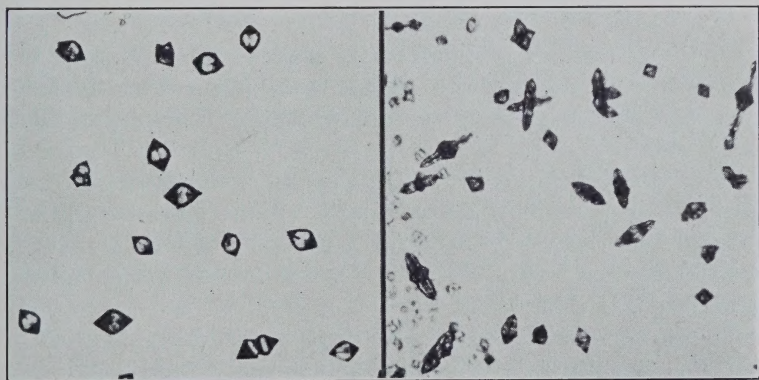


FIG. 148. Osmium Precipitated as Potassium Osmate. 100 $\times$.

FIG. 149. Osmium Precipitated as Potassium Osmate. 200 $\times$.

B—By Means of Thiourea — $SC(NH)_2$. — See pages 258–263.

C—Other Tests for Osmium.

(a)—Probably the most sensitive and characteristic test is the odor of the vapor of osmium tetroxide, which cannot be mistaken. It is violently irritating and attacks the mucous membranes, hence

great care must be exercised when handling even minute amounts of compounds of osmium.

(b)—Osmium compounds are easily reduced to the metal by most organic compounds. Hence care must be taken to exclude such materials when testing for osmium. This ease of reduction is the basis for the use of "osmic acid" in testing for fats and oils, with which it gives a black color.

(c)—Osmic acid dissolved in a little strong HCl gives with CsCl yellowish isotropic octahedra and plates of a double chloride of uncertain composition. A relatively high concentration of osmium is required, and the absence of too much water. The test appears to be of no value in routine testing, for in our experience it is uncertain and unreliable. Test drops which fail to yield a precipitate cannot be concentrated by heating because of the volatility of OsO_4 .

(d)—In acid solution osmium is precipitated, black, by metallic zinc, FeSO_4 , SnCl_2 , and many other reducing agents.

DETECTION OF IRIIDIUM AND PLATINUM

In the absence of osmium, alloys of both these elements are soluble in aqua regia. Both yield complex anions with the halogens, the potassium-group salts of which are characteristic and easily obtained.

It is assumed in this discussion that the material has been repeatedly evaporated with aqua regia. Under these conditions the solution to be tested will be a HCl solution of H_2IrCl_6 or H_2PtCl_6 or a mixture, and any IrCl_4 or PtCl_4 first formed will have been converted into chloro-acids.

To the moderately dilute test drop add KCl by Method I. K_2PtCl_6 separates in isotropic orange-yellow octahedra (see Potassium, page 66); K_2IrCl_6 in tiny dark red isotropic octahedra. These two salts form isomorphous mixtures. A similar salt is formed with RbCl (Fig. 147, page 269).

It has already been pointed out that the solubilities of the alkali salts of H_2PtCl_6 decrease with a rise in the atomic weight of the alkali, *i.e.*, K, (NH_4) , Rb, Cs, (Tl^+) . The sensitivity of the reaction for platinum is therefore increased by substituting for potassium any one of this series, but the size of the crystals formed is also greatly diminished, so that with thallium only a fine granu-

lar precipitate is obtained but the sensitivity is increased over a hundred fold (Behrens).

Platinum is differentiated from iridium by the difference in the color of the salts, and by the fact that $(\text{NH}_4)_2\text{IrCl}_6$ is much more soluble than $(\text{NH}_4)_2\text{PtCl}_6$ and forms a reddish solution instead of a yellow precipitate. Furthermore, whereas very dilute solutions containing platinum as H_2PtCl_6 give an instantaneous precipitate with TINO_3 consisting of tiny yellowish octahedra, solutions containing H_2IrCl_6 are reduced by the thallium salt and yield a blackish green flocculent precipitate but no crystals.

Palladium as H_2PdCl_6 gives K_2PdCl_6 in brownish prisms; but K_2PtCl_6 precipitated in the presence of palladium retains its octahedral form, and the crystals instead of being yellow are brown. Boiling a dilute solution before the addition of the alkali chloride will generally cause decomposition and reduction and precipitation of the palladium chloride. A similar treatment is without effect upon H_2PtCl_6 .

Platinum may be differentiated from iridium and palladium by conversion into a cupric salt of platino-tetrammine chloride ($\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{CuCl}_2$ or $\text{Pt}(\text{NH}_3)_4 \cdot \text{CuCl}_4$).¹³

The H_2PtCl_6 must first be reduced by SnCl_2 . This can be accomplished by dissolving metallic tin in HCl and adding tiny drops to the test drop until its yellow color has completely changed to brown; a slight excess of SnCl_2 is not objectionable. Add a few fragments of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$; stir until dissolved, warming gently if necessary. Cool and add an equal quantity of NH_4Cl . If the reduction has been complete no yellow octahedra should be precipitated. Now apply strong NH_4OH (1 : 1) by Method I. Hold the preparation over white paper. A blue-violet precipitate will be seen to have been produced. Under the microscope it will be found to consist of a great mass of slender needles, one end of which develops into feathery tufts like the tassels of maize or sugar-cane. On standing there may form, at the circumference of the drop, long, thin prisms with square or oblique ends singly or in tufts or radiates. This reaction is specific for platinum (Fig. 146, page 269).

If a palladium salt is substituted for the copper salt similar crystals are obtained but they are brownish. In mixtures containing both copper and palladium the blue-violet becomes a dirty

¹³ Werner. See Urbain: *Chimie des Complexes*, pp. 225, 234.

violet. Chlorides or other divalent elements can take the place of copper or palladium but the reactions obtained are not so readily interpreted.

In test drops rather high in platinum the reduction can be brought about by adding metallic tin. Part of the platinum is deposited upon the tin as a dark colored coating, part is reduced to platinous chloride, for SnCl_2 does not completely reduce H_2PtCl_6 to metallic platinum.

It is obvious that the formation of this copper salt of platinotetrammine is a means of distinguishing between platinous and platonic salts, or to put it more correctly, between chloroplatinic acid and platinum chlorides.

Iridium gives no precipitate and no color with thiourea, but in the case of platinum the crystals formed are very characteristic and the reaction is a sensitive one. (See pages 258-263.)

Separation and Identification of the Platinum Group in Alloys (and Minerals).¹⁴—The finely divided material is extracted repeatedly with hot concentrated HCl to remove iron and other easily soluble metals.

The residue is repeatedly treated at room temperature with slightly diluted aqua regia as long as a yellow solution is obtained. The solution is tested for gold.

The residue insoluble in cold aqua regia is boiled with concentrated HCl , 6 parts, concentrated HNO_3 , 1 part, as long as anything dissolves. Solution: platinum, iridium, rhodium, palladium, members of the copper group and perhaps gold. The residue will contain any ruthenium, iridium or osmium. (If iridium is absent osmium will have been driven off.) If iridium is present, test the residue as directed under Osmium, page 270 (and also make a special distillation for osmium).

The solution containing platinum, iridium, rhodium or palladium, etc., is evaporated almost to dryness and dissolved in water.

Precipitate the platinum and iridium with NH_4Cl . Add alcohol, filter or centrifuge, wash with alcohol the insoluble residue consisting of $(\text{NH}_4)_2\text{IrCl}_6$ and $(\text{NH}_4)_2\text{PtCl}_6$.

Acidify with aqua regia and concentrate the united filtrates until crystals begin to form. Test a large drop by means of

¹⁴ This outline follows in the main the procedure of Behrens, with modifications taken from Noyes and Bray.

NH_4OH , page 273. If both rhodium and palladium are present, the double chloride of rhodium and pallado-tetrammine will be obtained. Usually crystals of the chloride of pallado-diammine separate first, followed by those of the palladium-rhodium compound.

Iridium and rhodium can be separated from the copper group by treating with NaNO_2 in acetic acid solution, warming and adding NaOH . Iridium and rhodium form soluble nitrites, but the copper group is precipitated. Filter, add HNaCO_3 to precipitate any lead present. Filter. Evaporate the filtrate with HCl , dissolve in water and add Na_2CO_3 and bromine, and filter off the precipitated iridium and rhodium oxides. Filter, wash and test after solution in aqua regia.

The residue from the concentrated aqua regia, consisting of ruthenium and "Osmiridium," is fused with KOH and KClO_3 and tested for osmium as on page 270, and for ruthenium as on page 256.

An alternative separation is that of Noyes and Bray:

The material is brought into solution by heating with concentrated HBr ; bromine is added from time to time until the reaction is complete. The solution is concentrated and transferred to a suitable distilling tube, a little water and HNO_3 (16 *N*) added. Distil slowly until bromine vapors are no longer seen, collecting the distillate in KOH kept cold with ice water. Add Na_2O_2 to the distillate until it is colorless, and continue the distillation. Osmium passes over as OsO_4 and is fixed by the alkali. Set the distillate aside, and place a fresh solution of alkali to receive a distillate. Add to the contents of the distilling tube an equal volume of HClO_4 (9 *N*) and continue the distillation. Ruthenium passes over as RuO_4 .

Test the first distillate by adding alcohol. (See page 270.) (If osmium has passed over, the distillate will be yellow or brown.)

To a portion of the second distillate (orange or red) add alcohol; black metallic ruthenium is precipitated. To another portion add HCl ; a hydrous oxide is precipitated, centrifuge or filter and dissolve in aqua regia. Evaporate and test with thiourea. (See page 258.)

For the remaining elements rhodium, palladium, iridium, platinum, and gold dissolve the material in aqua regia, concentrate. Extract the HAuCl_4 with ethyl acetate.

To the aqueous liquid add HCl , evaporate almost to dryness,

take up with water, add NH_4Cl , and filter off the precipitate of $(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{NH}_4)_2\text{IrCl}_6$. The filtrate contains palladium and rhodium (and iridium, the latter in traces).

Evaporate the ethyl acetate, ignite the residue, dissolve in aqua regia, and test for gold. (See page 278.)

Dissolve the NH_4Cl precipitate in aqua regia, concentrate, and test for platinum and iridium. (See pages 272, 273.)

Evaporate the filtrate containing palladium and rhodium, boil with aqua regia, concentrate, and test for palladium (see page 264) and for rhodium. (See page 263.)

None of the above separations are quantitatively exact, but are usually sufficiently sharp to permit identifications save when only a "trace" of a given element is present.

In general it may be said that separations are seldom necessary if judgment is used in the selection of direct tests upon the material in question.

One of the latest and most comprehensive schemes for the separation of the metals of the platinum group is given below. According to its author the separations are quantitative. The chief drawback to its general use is that the reagent α furildioxime is not obtainable in commerce but must be prepared by the analyst.¹⁵ Aside from difficulties in handling alcoholic solutions in microscopical qualitative analysis the scheme is an excellent one and will be found dependable.

Scheme for the Qualitative Analysis of the Platinum Metals.¹⁶ —

To a solution of the chlorides in dilute HCl (1 : 12) add a *very* slight excess of a one per cent alcoholic (95%) solution of dimethylglyoxime. Decant, filter or centrifuge. — Filtrate I. Precipitate *a*.

Precipitate *a*. Pd

See page 264. Ignite, dissolve in aqua regia, evaporate. Test with Thiourea. (See page 258.)

Filtrate I. Pt; Rh; Ru;
Ir; Os

Add a slight excess of a two per cent alcoholic solution of α furildioxime, then a little alcohol ($\frac{1}{10}$ total volume). Filter or centrifuge. Filtrate II. Precipitate *b*.

¹⁵ See Soule: *Jour. Amer. Chem. Soc.* **47**, 981 (1925).

¹⁶ Based upon Method of Ogburn: *Jour. Amer. Chem. Soc.* **48**, 2493, 2507 (1926); *Jour. Chem. Education* **5**, 1383 (1928).

Precipitate <i>b</i> .	Pt	(See page 272.) Ignite. Dissolve in aqua regia and test with KCl. (See page 273.)
Filtrate II.	Rh; Ru, Ir, Os	Evaporate almost to dryness. Add HCl and NaClO ₃ to destroy the oximes. Add alcoholic KNO ₂ avoiding an excess. Allow to stand a long time. Centrifuge. Filtrate III. Precipitate <i>c</i> .
Precipitate <i>c</i> .	Rh	(See page 263.)
Filtrate III.	Ru; Ir; Os	Boil until all oxides of N cease to be evolved and all alcohol has been expelled. Acidify with HCl. Evaporate almost to dryness. Add alcoholic NaOH. Boil. Centrifuge. Filtrate IV. Precipitate <i>d</i> .
Precipitate <i>d</i> .	Ru	As Ru ₂ O ₃ ·3 H ₂ O. (See page 256.)
Filtrate IV.	Ir; Os	Evaporate to expel all alcohol. Acidify with dilute HCl. Add metallic zinc. When all reaction has ceased filter or centrifuge. Filtrate V. Precipitate <i>e</i> .
Precipitate <i>e</i> .	Ir, Os	As metallic Ir, and metallic Os. Treat with a solution of freshly prepared NaOCl. Filter or centrifuge. Filtrate V. Precipitate <i>f</i> .
Precipitate <i>f</i> .	Ir	Dissolve in aqua regia. Test with KCl (see page 272); and with aniline hydrochloride. (See page 268).
Filtrate V.	Os	Acidify with HCl. Add metallic zinc. Metallic Os is precipitated. Dissolve in aqua regia. Test with thiourea (page 258), or precipitate as potassium osmate (page 270).

DETECTION OF GOLD

The material to be tested will probably have been brought into solution by means of aqua regia, hence it is assumed in the following tests that gold is present as chloroauric acid, HAuCl_4 . On heating, this compound may be reduced to AuCl , a white salt insoluble in water, or if heated still further metallic gold is obtained. Hence care must be exercised when it is necessary to expel an excess of aqua regia.

A—Detection through Reduction to Colloidal Gold.

(a)—Method of Cole.¹⁷ — To the test drop, which should be as free as possible from HNO_3 and from HCl , add a SnCl_2 -pyrogallol carrying viscose-rayon fiber about 5 mm. long, laying it half in, half out of, the test drop. Examine it from time to time, allowing the drop to pass completely to dryness by spontaneous evaporation. If gold is present, the fiber turns red, violet, or blue, depending upon concentrations.

Free mineral acids greatly retard the reaction. Alkalis and oxidizing agents must be absent. Compounds that react energetically with SnCl_2 must also be absent.

Silver imparts a brown color to the fiber when in large amount, but does not mask the color of the gold unless the latter is present only in traces. Chromates, bichromates, and permanganates color the fiber brown, and if gold is also present the color of the fiber becomes a brownish red or purple, rendering the interpretation of the test doubtful.

Molybdates color the fiber blue but never bluish-red, violet or red.

The bluish-red, violet, or red color appears to be specific for gold, and permits the detection of gold in the presence of chlorides of the other elements.

The metals of the platinum group do not interfere.

The reagent fibers are prepared as follows:

“ 10 grams of SnCl_2 crystals are dissolved in 95 cc. of distilled H_2O and 5 cc. concentrated HCl , and filtered; 10 grams of white pyrogallol are added to the filtrate, a little at a time, with constant stirring. Fine viscose-rayon fibers are intro-

¹⁷ *Philippine Journ. Sci.* **21**, 361 (1922).

duced into the solution and the preparation is heated on the water bath for ten minutes. The fibers are then removed, washed well with distilled water, and dried by pressing between filter paper."

The fibers thus treated keep well and are very sensitive.

(b)—Method of Donau.¹⁸ — Raw, true silk fibers are purified by soaking in 10 per cent KOH for several hours, washed thoroughly and then treated with SnCl_2 and pyrogallol as described above, washed, dried, and used to test for gold. The behavior of the treated fiber in the presence of gold is exactly the same as that of the viscose-rayon fiber, but the latter is more sensitive and can be kept in serviceable condition for a longer time

B—By Means of Thallous Nitrate — TlNO_3 .

Compound Formed — $\text{TlAuCl}_4 \cdot 5 \text{H}_2\text{O}$.

If the material to be tested has been brought into solution with aqua regia, it should be evaporated repeatedly with concentrated HCl to drive off all HNO_3 . The solution is then carefully evaporated substantially to dryness to free it from HCl.

To the faintly yellow test drop add several crystals of TlNO_3 . The reagent almost immediately becomes covered with a coating of bristling yellow needles which rapidly grow into long thin prisms with oblique ends. Lemon-yellow rhombiform plates also abound; they have an acute angle of about 82° and extinguish at an angle of approximately 28° with their elongation. Short stout prisms with beveled or truncated ends are formed on long standing. Often, remarkable very long and curving trichites are obtained (Fig. 140, page 259).

In view of the large number of double chlorides into the composition of which thallium enters, this beautiful reaction has little value in the routine analysis of unknown substances. It is useful as a confirmatory test when applied to material which has been isolated by processes yielding a gold salt freed from most impurities.

Platinum and iridium give exceedingly minute octahedra.

Palladium gives radiates, stars and lichen-like masses. (See Palladium, page 266.)

C—By Means of Silver Nitrate and Rubidium Chloride. — See page 84.

¹⁸ *Monatsh.* **25**, 545 (1904).

D—By Means of Ammonium Thiocyanate — NH_4SCN .*Compound Formed* — $\text{Au}(\text{SCN})_3$.

To the well-diluted test drop add the reagent by Method II, page 32.

$\text{Au}(\text{SCN})_3$ separates in orange-red, branching dendrites united in aggregates resembling tufts of moss (Fig. 153, page 299). The reaction is specific for gold in the absence of other elements yielding insoluble or difficultly soluble thiocyanates, but since these are many this reaction is limited in its applications. It is of value as a confirmatory test when gold has been separated from interfering elements.

When $(\text{NH}_4)\text{SCN}$ is used, some of the gold may be reduced to the metallic state (colloidal), appearing as a red or blue colored zone some distance from the reagent.

DETECTION OF THE RARE EARTHS

This group of rare elements, whose properties place them in the Third and Fourth Groups of the Periodic System but whose atomic weights (in part) require that they be set apart in a series by themselves, constitute one of the most intricate and difficult separation problems confronting the chemist-analyst. Several of the now so-called "elements" in the series are probably not simple substances, and it is doubtful whether any of them have been prepared in a really pure state.

	La 139	Ce 140	Pr 141
Nd 144		Sm 150	Eu 152
Gd 157	Tb 159	Dy 162	Ho 163
Er 168	Tu 169	Yb 174	Lu 175

The relationships of those of the "rare earths" not found in the Periodic Classification of the Elements as shown on page 400 can

be expressed by the above tabulation. The atomic weights, as given, are approximate only.

If the problem of separation and identification is so difficult on a large scale that chemists have struggled with it for many years with only a modicum of success, how infinitely more complicated must the problem be when attempting analyses on a "micro" scale.

Many excellent separation methods have been described, but none are sharp. None of the precipitations are quantitatively complete; always a little of the precipitated substance is left behind in solution and always the precipitate carries down with it other substances. Thus the purification methods at our command must be, for the most part, some system of fractionation, but fractionating of the kind required is impracticable when dealing with very small amounts of material.

It is true that Behrens has reported¹⁹ that he had considerable success in identifying a number of the rare earths by microscopical reactions, and that R. J. Meyer²⁰ has been similarly optimistic, but we have had doubtful success, even though one of us has had some years of experience in "rare-earth" research.

There is no question that most of the individual substances composing the group commonly termed the "rare earths" when tested in the form of their "pure" salts give crystal reactions sufficiently different in character to enable an experienced analyst to differentiate between them. He may even be successful when dealing with mixtures he has made up. But it is a very different matter when the analyst is confronted with materials of which he has no previous knowledge.

We must still have recourse to the spark, arc, and absorption spectra, or to X-ray spectrographic methods, for the identification of the "rare earths." The "earths" are too closely related and form isomorphous mixtures far too readily to permit dependable identification methods to be based upon crystal habit and optical properties.

Because the authors do not consider the known "micro" tests sufficiently trustworthy in the case of the "rare-earth"

¹⁹ Behrens: Ein Beitrag z. Kenntnis d. Metalle d. Ceriumgruppe. *Arch. néerland.* (2) **6**, 67 (1902). See also Behrens-Kley, *op. cit.*

²⁰ Meyer, R. J.: Der mikroskopische Nachweis d. selten Erden. *Zeit. f. anorg. Chem.* **33**, 31 (1902).

group as a whole they have given below a mere outline of properties, crystal habits and separation methods.

Classification.

<i>Cerium Group</i>	{	Scandium	}	Sulphates practically insoluble in saturated solution of K_2SO_4
		Thorium		
		Lanthanum		
		Cerium		
		Praseodymium		
		Neodymium		
		Samarium		
		Erbium		
Holmium				
<i>Terbium Group</i>	{	Europium	}	Sulphates moderately soluble in saturated solution of K_2SO_4
		Gadolinium		
		Terbium		
		Samarium		
<i>Yttrium Group</i>	{	Yttrium	}	Sulphates readily soluble in saturated solution of K_2SO_4
		Ytterbium		
		Lutetium		

It is customary to start with precipitation by an excess of oxalic acid in a solution rather strongly acidified with HCl. The precipitation is not complete.

The filtered and well-washed oxalates are ignited and the oxides dissolved in HNO_3 .

A number of the "rare earths" can be identified by their absorption spectra. The observations can be made by light transmitted through their solutions, through their crystals, or by observations made upon light reflected from them in the solid or liquid state.

It must be borne in mind, however, that the absorption spectra of different salts of the same "earth" will vary unless the dilution is great, and that an excess of acid in the solutions will displace the absorption bands.²¹ (See in this connection, *Vol. I*, page 187).

Dysprosium, Erbium, Europium, Gadolinium, Holmium, Neodymium, Praseodymium, Samarium and Thulium give absorption bands.

²¹ See Kayser: *Handbuch der Spectroscopie* III, 427-453. (Hirzel, Leipzig, 1905).

Formànek: *Die qual. Spektralanalyse anorganische Körper*, (Mückenberg, Berlin, 1900).

Baly, E. C. C.: *Spectroscopy* (Longmans, N. Y., 1924).

The wavelengths in Ångström units of the most important of these bands are as follows:

Dysprosium (Chloride):

4740; (4530–4500); (Urbain)

Erbium (Nitrate): 16 bands.

5232; 4875; 4499; (Formànek)

Europium.

5900; 5700; 5350; 5250;

4690; 3995; 3855; (Demarçay)

Gadolinium (Nitrate):

(3500–3390); (3300–2890); (2200) (H. D. Jones)

Holmium (Nitrate):

6405; 5363; (Dennis and Dales)

Neodymium (Nitrate); 9 bands:

7291; (5979–5759); (5222–5209); 4277; (Formànek)

Thulium (Nitrate):

6832; (Dennis and Dales)

Since uranium is very apt to be present in “rare-earth” solutions, unless special precautions have been taken to eliminate it, the analyst should be on his guard so as to recognize the absorption spectrum of its nitrate solution.

Uranium (Nitrate):

4705; 4867; 4545; 4425; 4290; 4150; (Formànek)

One of the most comprehensive of the many separation schemes which have been proposed is that of Noyes and Bray.²²

Only that part dealing with the “rare earths” is here given:

The earths are converted into insoluble fluorides by HF.

The insoluble “rare-earth” fluorides are treated with HF containing an excess of NH_4F .

Scandium fluoride is dissolved.

The insoluble fluorides are treated with concentrated H_2SO_4 , heated until SO_3 fumes appear, water added and NH_4OH added in slight excess. Filter, wash and dissolve the precipitate in $\text{HC}_2\text{H}_3\text{O}_2$. Evaporate, add HNO_3 , KClO_3 , and KIO_3 .

ThIO_3 , CeIO_3 are precipitated. Filter.

²² *Op. cit.*

To the filtrate from thorium and cerium add NH_4OH , filter, dissolve in HCl , and add K_2CO_3 .

Double carbonates of La, Pr, Nd, Sm, Eu, Y, Yt, Lu are precipitated. The salts precipitated have the general formula $\text{K}_2\text{CO}_3 \cdot \text{MCO}_3$.

The solution from the K_2CO_3 solution contains Y group, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu and traces of Nd, Sm, Eu. HCl is added and NH_4OH . The precipitate formed is dissolved in HCl , evaporated and formic acid and ammonium formate added.

Nd, Sm, Eu are precipitated as formates together with some of the yttrium group.

Y, Yt, Lu form soluble formates and remain in solution.

The further separation as advocated by Noyes and Bray, by fusion with NaNO_3 , is impracticable on a micro-scale.

Behrens states that the best reagent for the separation of neodymium from praseodymium is by fractionating cerium-free material with ammonium succinate in nitrate or chloride solutions.

The precipitate obtained, consists in

- Fraction I, of Nd and much Sm
- II, almost entirely of Nd
- III, of Nd and Pr, and a little Sm
- IV, almost entirely of Pr
- V, of Pr and La

The reagents which have been proposed for the "micro" identification of the "rare earths" are as follows:

- Ammonium succinate
- Formic acid and ammonium formate
- Iodic acid and potassium iodate
- Lactic acid
- Oxalic acid
- Potassium carbonate
- Potassium ferrocyanide
- Potassium sulphate

None of these reagents give sharp definite reactions with mixtures of the "rare earths."

It is imperative that the analyst shall have experimented with

pure materials and with mixtures and that he shall have conscientiously carried through the various separation methods if he is to avoid serious errors when dealing with materials of wholly unknown "rare-earth" content.

The authors are inclined to go a step farther and state that until an analyst has obtained and worked upon materials of which he himself knows nothing but whose composition is known to others so that he can thus check his findings he should not have the temerity to attempt a qualitative analysis of "rare earths," minerals or products.

CHAPTER XI

THE DETECTION OF ANIONS

The identification of the anion of a salt is more difficult and more complicated than is the search for its cation, and in mixtures the problem becomes even more intricate and is almost sure to tax the chemical knowledge and resourcefulness of the analyst.

Tests for cations are ordinarily quite specific and an "element" can be readily detected, no matter with what "acid" it is combined, but there are fewer specific tests for anions as such and there is the possibility of conversion to another anion. Moreover, the behavior of an anion toward reagents is largely influenced by the nature of the cation with which it is combined, so that the identification of the anion of a given salt must not infrequently turn upon the identification of its cation also, before the problem can be solved.

The problem becomes even more involved when the analyst is confronted with the task of devising a means of identifying a complex ion and of deciding whether he has to deal with a true double salt or a complex.

For the purposes of qualitative analysis, the "elements" can be classified into relatively small and quite distinctive groups, but such distinctive groupings are not practicable with the acids. Even the most satisfactory of these — the Bunsen-Treadwell classification — leaves much to be desired.

Wholly aside from the absence of satisfactory "Tables" for the detection of the anions, and the lack of specific identity tests, their recognition is the more difficult when the analyst bases his deductions wholly upon the properties of the cations he has found, and fails to consider the probable chemical behavior of the compound in question in its entirety. This may, perhaps, be a distinction too finely drawn, but it is nevertheless quite germane to the problem and always has a decided bearing upon the solution of a complex analytical problem.

A further caution is necessary in testing for anions. The ana-

lyst must not fail to consider the possibility of a reaction between a cation in the unknown and an anion in the reagent. For example, when using the Bunsen-Treadwell classification the addition of BaCl_2 may cause a precipitate of chlorides of Ag^+ , Pb^{++} , Hg^+ , or Tl^+ , and such a precipitate may be mistaken for an insoluble or difficultly soluble salt of Ba^{++} . The analyst may thus be led into the error of concluding that an anion is present which gives a precipitate with Ba^{++} .

In general the identification of cations must go hand in hand with the detection of anions. It is never safe to base conclusions upon results obtained by blindly following a "scheme" of analysis.

The recognition of the true nature of a given crystalline compound lies not so much in the identification of the cations and anions present as in reaching a decision as to exactly how they are combined; in other words, is the material a mechanical mixture, an isomorphous mixture, a double or a mixed salt, or a salt containing complex ions? The solution of the problem rests as much or more upon physico-chemical experiments and crystallographic properties as upon the addition of reagents. This phase has already been discussed in *Vol. I*, page 360, to which the reader is referred.

The problem of complex ions is not easily solved. There are many reasons for believing that their existence in materials is much more general than is commonly supposed. In many instances an equilibrium exists between the complex ion and the simple anions and cations which compose it, so that either may be exhibited in analytical testing. The effective concentrations of a number of anions may be markedly lowered by their being "locked up" in complex ions; the complexes may dissociate partially, according to the mass law, if the concentration of the simple anion is lowered. The analyst must be guided by his general knowledge of chemistry, by the properties of the compound in hand, or by actual experimental electrolysis. Unfortunately the latter can be successfully undertaken by experienced workers only, and is fraught with complications. We still lack data in many cases as to whether a compound is a double salt or a salt of a complex ion.

To facilitate discussion and expedite analyses, the authors have adopted the Bunsen-Treadwell classification of the acids. This classification is based upon the behavior of the commoner anions

toward silver nitrate and toward barium chloride in neutral and in nitric acid solutions.

No system based upon solubilities can be wholly satisfactory. A very minute amount of a precipitate recorded as "slightly" soluble may appear to be "readily" soluble if treated with sufficient solvent to bring it into solution. Moreover, an "insoluble" precipitate may be peptized by materials present and thus appear to be soluble. Furthermore, extremely high concentrations may result in precipitates of salts which would normally be considered readily soluble.

An equal difficulty arises in regard to the color of a precipitate, for if but faintly colored and in small amount the precipitate will not be recognized as colored. A good example is that of AgI , which is so faintly yellow that in "micro" amounts it will be classed as colorless. Faint colors must be observed by reflected light after the precipitate formed has been collected into a little heap. This can usually be accomplished by pushing the precipitate together so as to mass it just outside the circumference of the drop, using a drawn-out glass rod or tiny platinum spatula for the purpose. It is best to compare appearances upon a white and upon a dark background. The variety of colors listed for each precipitate may be ascribed to the range of particle-size. The first particles to separate are likely to be so fine as to appear very pale in hue even when larger crystals are intensely colored or almost opaque.

SILVER NITRATE GROUP I

The Silver Salt is Insoluble in Water and in Strong Nitric Acid, and is Not Perceptibly Crystalline nor Colored.

Cl^-	Chloride	May separate in crystals recognizable as tiny octahedra.
BrO_3^-	Bromate	May separate in crystals recognizable as tiny crosses and prisms.
Br^-	Bromide	Granular, or very tiny octahedra.
CN^-	Cyanide	Granular or fine prisms.
I^-	Iodide	Granular.

OCl^-	Hypochlorite	Silver hypochlorite is soluble in water, but through decomposition AgCl and AgClO_3 are formed.
$\text{Fe}(\text{CN})_6^{4-}$	Ferrocyanide	Precipitate turns red or brown with HNO_3 .
SCN^-	Thiocyanate	Precipitate soluble in conc. HNO_3 but not in dilute.

SILVER NITRATE GROUP II

A Colored Precipitate is Formed upon the Addition of Silver Nitrate.

(a)–The precipitate is red or brown.

AsO_4^{3-}	Arsenate (ortho)	Granular; irregular cryst. grains; plates and tablets; dendritic masses. Difficultly soluble in cold HNO_3 ; readily soluble in hot HNO_3 . Soluble in NH_4OH .
CrO_4^{2-} ; $\text{Cr}_2\text{O}_7^{2-}$	Chromate; Bichromate	Granular; rectangular and non-symmetrical 6-sided plates; acute rhombs; aggregates of pleochroic broken scales; difficultly soluble in cold HNO_3 . Soluble in hot HNO_3 . Soluble in NH_4OH .
$\text{Fe}(\text{CN})_6^{3-}$	Ferri cyanide	"Amorphous." Difficultly soluble in HNO_3 .
IO_4^-	Periodate	Yellow at first, becoming brown; hexag. rosettes and platelets.
$\text{S}_2\text{O}_3^{2-}$	Thiosulphate	White "amorphous" ppt. changing to yellow, then to dark brown (Ag_2S). Solubility in HNO_3 indeterminate owing to presence of precipitated sulphur.
S^{2-}	Sulphide	Brown, becoming black. "Amorphous." Soluble in HNO_3 .
MnO_4^-	Permanganate	Solution was pink or red. From very concentrated solutions a black cryst. ppt. Thin plates violet-red.

$(\text{H}_2\text{PO}_2)^-$	Hypophosphite	There is first formed a heavy white "amorphous" or granular ppt. which turns brown or black (Ag).
(b)-The precipitate is yellow.		
AsO_2^- ; AsO_3^{---}	Arsenite	"Amorphous"; granular or acicular; soluble in HNO_3 .
$\text{Fe}(\text{CN})_6^{---}$	Ferri cyanide	Rarely yellow, usually red or brown. "Amorphous." Difficultly soluble in HNO_3 .
IO_4^-	Periodate	Yellow, changing to brown on standing.
NO_2^-	Nitrite	Colorless needles unless in a mass, then yellowish green. Soluble in HNO_3 .
PO_4^{---}	Phosphate (ortho)	Granular; tiny dendritic stars crosses and radiates. Soluble in HNO_3 .
SiO_3^{--}	Silicates	May be yellow ppt. or ppt'g. of Ag_2O . If $(\text{SiO}_2)_x$ is precipitated, insoluble in HNO_3 . Colloidal Ag may be formed.
VO_3^- ; VO_4^{---}	Vanadates	"Amorphous"; readily soluble in HNO_3 .

SILVER NITRATE GROUP III

A White or Colorless Precipitate is Formed, and the Precipitate is Soluble in Nitric Acid.

(a)-The precipitate is usually crystalline.

$(\text{C}_2\text{H}_3\text{O}_2)^-$	Acetate	Pearly scales, thin plates and irregular prisms.
$(\text{MoO}_4^{--})?$	Molybdate	"Amorphous" or granular.
NO_2^-	Nitrite	Long slender needles. Yellowish-green.
$(\text{C}_2\text{O}_4)^{--}$	Oxalate	Granular; hexagonal plates; prisms.

$S_2O_8^{--}$	Persulphate	$Ag_2S_2O_8$ is readily soluble in water. The addition of $AgNO_3$ to the test drop is without effect for a few seconds; then there appears a copious separation of crystals of Ag_2SO_4 . Often the test drop turns brown, especially at its circumference.
SeO_4^{--}	Selenate	Skeletal forms; rhombs; prisms.
SO_4^{--}	Sulphate	Skeletal forms; rhombs; prisms.
$(C_4H_4O_6)^{--}$	Tartrate	Granular; rectangular tablets; short prisms.
$S_2O_3^{--}$	Thiosulphate	First white, changing to yellow to brown (Ag_2S). If much sulphur is set free ppt. will appear to be insoluble in HNO_3 .
WO_4^{--}	Tungstate (ortho)	"Amorphous" or granular.

(b)–The precipitate is not discernibly crystalline.

$B_2O_4^{--}(BO_2^-)$; $B_4O_7^{--}$	Borates	"Amorphous," curdy; granular.
CO_3^{--}	Carbonate	"Amorphous," granular; may become crystalline.
CNO^-	Cyanate	"Amorphous," becoming crystalline; fine needles; prisms.
IO_3^-	Iodate	"Amorphous." Acicular and radiating crystals in presence of HNO_3 .

SILVER NITRATE GROUP IV

The Silver Salt is Soluble in Water.

(a)–No precipitate is formed even in concentrated solutions.

ClO_3^-	Chlorate	
ClO_4^-	Perchlorate	
F^-	Fluoride	Partly decomposed by water with precipitation of Ag.
MnO_4^-	Permanganate	$AgMnO_4$ separates from highly concentrated solutions.
NO_3^-	Nitrate	

(b)–The silver salt has a solubility sufficiently low to separate from concentrated solutions.

$(C_2H_3O_2)^-$	Acetate	Pearly scales; thin plates, irregular prisms.
$B_2O_4^{--}$; $B_4O_7^{--}$	Borate	"Amorphous," curdy, granular.
SiF_6^{--}	Fluosilicate	Granular, becoming crystalline.
TiF_6^{--}	Fluotitanate	Granular, becoming crystalline.
ZrF_6^{--}	Fluozirconate	Granular, becoming crystalline.
SeO_4^{--}	Selenate	Skeletal forms, rhombs, prisms.
$S_2O_8^{--}$	Persulphate	A precipitate of Ag_2SO_4 is obtained. See Silver Nitrate, Group III, page 291.

BARIUM CHLORIDE GROUP I

The Barium Salt is Insoluble in Water, and Insoluble in Nitric Acid.

CrO_4^{--} ; $Cr_2O_7^{--}$	Chromate; Bichromate	$BaCrO_4$ is difficultly soluble in HNO_3 . Granular becoming crystalline; dendritic.
SiF_6^{--} ; TiF_6^{--} ; ZrF_6^{--}	Fluosilicate; Fluotitanate; Fluozirconate	Difficultly soluble in HNO_3 . Crystalline prismatic grains; spherocrystals, sheaves.
NO_3^-	Nitrate	$Ba(NO_3)_2$ is almost insoluble in HNO_3 , and of low solubility in water; crystals may separate from concentrated solutions and will not dissolve in HNO_3 .
IO_3^-	Iodate	Granular; fine prisms and crosses; difficultly soluble in HNO_3 .
SO_4^{--}	Sulphate	Granular, becoming crystalline plates, tablets, skeleton crystals.
SeO_4^{--}	Selenate	Similar to SO_4^{--} .
WO_4^{--}	Tungstate (ortho)	"Amorphous," granular. WO_3 is precipitated by HNO_3 .

BARIUM CHLORIDE GROUP II

The Barium Salt is Insoluble in Water but is Soluble in Nitric Acid.

AsO_4^{---}	Arsenate (ortho)	"Amorphous"; obtained in concentrated solutions only.
$\text{B}_2\text{O}_4^{--}(\text{BO}_2^-)$; $\text{B}_4\text{O}_7^{--}$	Borates	"Amorphous"; granular.
BrO_3^-	Bromate	From concentrated solutions. Prisms.
CO_3^{--}	Carbonate	Curdy, becoming crystalline; variable.
CrO_4^{--} ; $\text{Cr}_2\text{O}_7^{--}$	Chromate; Bichromate	Bright yellow, granular. Soluble in HNO_3 with difficulty.
CNO^-	Cyanate	Disks, sphero-crystals, aggregates of fine needles.
F^-	Fluoride	Granular.
SiF_6^{--} ; TiF_6^{--} ; ZrF_6^{--}	See Group I.	
$(\text{HPO}_3)^{--}$	Phosphite	Disks, crystalline grains.
IO_3^-	Iodate	Granular; stars; dendrites. Difficultly soluble in HNO_3 .
$(\text{MoO}_4)^{--}?$	Molybdate	"Amorphous," granular.
$(\text{C}_2\text{O}_4)^{--}$	Oxalate	Granular; dendritic.
PO_4^{---}	Orthophosphate	"Amorphous," granular.
PO_3^-	Metaphosphate	Trace of precipitate.
$\text{P}_2\text{O}_7^{----}$	Pyrophosphate	Gelatinous.
SO_3^{--}	Sulphite	Granular, becoming crystalline; dendritic.
$\text{S}_2\text{O}_8^{--}$	Persulphate	Precipitate in concentrated solutions only. May appear to be insoluble in HNO_3 because of presence of SO_4 .
WO_4^{--}	Tungstate (ortho)	"Amorphous," granular. HNO_3 causes separation of WO_3 .

BARIUM CHLORIDE GROUP III

No Precipitate is Obtained when Barium Chloride is Added to a Dilute Aqueous Solution.

$(C_2H_3O_2)^-$	Acetate	
AsO_4^{---}	Arsenate (ortho)	A precipitate is obtained in moderately concentrated solutions.
AsO_2^- ; AsO_3^{---}	Arsenites	
BrO_3^-	Bromate	Precipitate in concentrated solutions. Prisms.
Br^-	Bromide	
ClO_3^-	Chlorate	
Cl^-	Chloride	
CNO^-	Cyanate	Solubility low. Precipitate in moderately concentrated solutions.
CN^-	Cyanide	Solubility low.
$Fe(CN)_6^{---}$	Ferri cyanide	
$Fe(CN)_6^{----}$	Ferrocyanide	Precipitate of prisms and tablets in moderately concentrated solutions.
$(H_2PO_2)^-$	Hypophosphite	
I^-	Iodide	
NO_3^-	Nitrate	$Ba(NO_3)_2$ is difficultly soluble and may separate from concentrated solutions.
NO_2^-	Nitrite	
$S_2O_8^{--}$	Persulphate	Solubility low. May precipitate.
PO_3^-	Metaphosphate	
$(C_4H_4O_6)^{--}$	Tartrate	Solubility low. May precipitate.
SCN^-	Thiocyanate	
$S_2O_3^{--}$	Thiosulphate	A precipitate in all but very dilute solutions.

Before testing with $AgNO_3$ or $BaCl_2$, two very important steps are essential if time is to be saved and trouble avoided. First: determine the reaction of the solution to litmus. Free acids and free alkalis do not fall within the scope of the above groups. Second: attempt to obtain good crystals from the material in question

and ascertain their behavior between crossed nicols. (See *Vol. I*, Chapter IX.)

In the end, the *real identification* of the salt must rest largely upon its optical properties, for the mere detection of cations and anions in solution usually gives inadequate information as to the actual solid salt in hand. There may exist a number of distinct hydrates, and in double salts there may exist several combinations in which the ratios of one component to the other are very different. (See *Vol. I*, pages 345, 360.) Optical tests alone cannot, however, be the sole criteria upon which a final decision is based, except in special cases.

Free acids should first be converted into salts by evaporating with NH_4OH , if practicable, if not, by careful neutralization with NaOH and evaporation.

Alkaline hydroxides are recognized through their general behavior, their strong alkaline reaction, their precipitation of Ag_2O or a hydrous oxide, and the identification of the metallic element present.

Having obtained an indication as to what anions are possibly present, apply to a series of test drops a specific test for each anion that may be present. In dealing with mixtures, separations of groups may be advantageous; these may be carried out macroscopically, or by means of micro-filtrations, decantation, distillation, etc.

Borates — BO_2^- , $\text{B}_4\text{O}_7^{--}$. — All borates are at least slightly soluble in water; those of the alkalis are readily soluble. The borates of the alkaline earths are as a rule more soluble in cold than in hot water.

The borates with which the analyst will come in contact are derived from orthoboric acid H_3BO_3 , metaboric acid HBO_2 , and pyroboric or tetraboric acid $\text{H}_2\text{B}_4\text{O}_7$. Few orthoborates are known, hence practically all borates commonly met with are meta- or pyro-borates.

With the exception of the alkali borates, few borates are stable in solution.

The detection of borates turns upon the identification of boron by means of viscose-rayon fibers impregnated with turmeric. (See Boron, page 156.)

An indication of the possible presence of boron can be obtained

by testing with NH_4HF as explained under Sodium (Method C, page 63. See also Boron, Method B, page 158). Silicon, titanium and zirconium must be absent. To obtain a separation of sodium fluoborate the test drop must be concentrated.

(a)-Group Reactions.

1-With AgNO_3 in all but very dilute solutions there is immediately formed a white curdy "amorphous" precipitate having a tendency to become granular, but no definite crystals are formed.

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields nothing more than a white granular precipitate not perceptibly crystalline.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ produces no precipitate save in very concentrated solution and then a slight turbidity results.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a curdy white precipitate, becoming granular.

5- $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ produces no precipitate and no crystals separate on standing.

Note. At present we have no specific reactions for borate ions, but must rely upon the detection of boron and a study of the crystallography and optical properties of the compounds under examination.

Carbonates — CO_3^{--} ; $(\text{HCO}_3)^-$. — The carbonates of sodium and those of the Potassium Group are readily soluble in water. Li^+ and Tl^+ form somewhat difficultly soluble carbonates. The normal carbonates of most of the other elements are either insoluble or difficultly soluble in water, but are partly (sometimes completely) soluble in water charged with CO_2 , due to their conversion into "bicarbonates," *i.e.*, salts of the anion $(\text{HCO}_3)^-$.

The carbonates of NH_4^+ , Rb^+ and Cs^+ are easily soluble in alcohol but none of the other common carbonates are soluble in this liquid.

The detection of carbonates is based upon the fact that they are readily transformed by acids, CO_2 being given off with effervescence.

The test for effervescence is made as described on page 39. Merely the appearance of gas bubbles in the gelatin cannot be taken as proof of the presence of CO_2 . CO_2 must be tested for by evolution and absorption in a hanging drop of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Absorption in a solution of this reagent gives rise to the formation

of acicular crystals, singly and in irregular aggregates, globulites or highly refractive rhomboidal grains.

Cyanates may also give off CO_2 when treated with an acid.

When dealing with a solution, one or more drops should be evaporated to dryness in the crucible (See Fig. 6, page 15), covered with asbestos fibers, acid added, and the CO_2 evolved tested with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

(a)–Group Reactions.

1–With AgNO_3 both carbonates and bicarbonates yield a heavy white “amorphous” precipitate soon becoming granular; in the outer zone tiny colorless angular grains appear, and the outer edge of the precipitate mass becomes distinctly granular. In a number of restricted areas, disks, rosettes, and hexagonal plates are formed but these crystals always remain very small. They are, however, highly refractive and strongly birefringent. As the test drop passes to dryness the mass of “amorphous” precipitate acquires a distinct cream color, due to the formation of a small amount of Ag_2O .

2–With $(\text{HCO}_3)^-$, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a slight sandy precipitate consisting of tiny crystalline grains of irregular shape; but with CO_3^{--} there is first formed a thick, heavy, somewhat curdy precipitate in which crystallization starts almost at once. Tiny crystalline grains are formed and moss-like, many-branching, radiating dendritic aggregates. Tiny dendritic masses are also abundant.

3– $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives no precipitate, and no crystals separate on standing when the reagent is added to solutions of alkali bicarbonates, but with normal carbonates (CO_3^{--}) a white flocculent “amorphous” precipitate is obtained that rapidly changes into very tiny rhombohedra. Eventually the entire precipitate becomes converted into strongly birefringent crystalline granules (Fig. 72, page 113).

4– $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ does not differentiate between CO_3^{--} and $(\text{HCO}_3)^-$ save that in the latter case the development of recognizable crystal forms is more rapid and the aggregates are of larger size. A heavy white “amorphous” precipitate is first formed. Tiny irregular colorless crystalline grains appear and tiny dendritic aggregates can be found in certain small areas. These branching aggregates become more and more numerous and assume shapes more like tufts of grass than moss, that is to say,

that the branches are straighter and smoother than in a moss-like clump. They are also more fan-shaped, and are therefore one-sided radiates.

5-Tl(C₂H₃O₂) gives no precipitate and no separation of crystals with (HCO₃)⁻, but with CO₃²⁻, colorless, long slender needles are formed that soon stretch completely across the field (Fig. 150, page 299). These needles may become prismatic and extinguish at about 5° with their elongation. Long slender thin plates with terminal angles of about 80° are also formed. The crystals are highly refractive, strongly birefringent, and exhibit brilliant polarization colors. They are more soluble than the acicular crystals obtained with PO₄³⁻ (Fig. 159, page 311), are formed more slowly as a rule, and tend to separate at the circumference of the test drop rather than at the zone of entrance of the reagent. Obviously the differences in the phenomena observed will depend upon relative concentrations.

DETECTION OF THE ANIONS OF THE NITROGEN GROUP

NO₃⁻, NO₂⁻; CN⁻; CNO⁻; SCN⁻; Fe(CN)₆³⁻; Fe(CN)₆⁴⁻

Logically these ions should be discussed as four separate groups: (1) NO₃⁻ and NO₂⁻; (2) CN⁻ and CNO⁻; (3) SCN⁻; (4) Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻; actually they have little in common and form five groups from the viewpoint of microscopic qualitative analysis.

Nitrates — NO₃⁻. — All normal nitrates are water-soluble. Most basic nitrates are difficultly soluble or insoluble. A few normal nitrates are decomposed by water and an insoluble basic nitrate is produced (*e.g.*, BiONO₃, SbONO₃).

Many nitrates are less soluble in HNO₃ than in pure water; the most striking of these are the nitrates of Cd⁺⁺, Pb⁺⁺, and Ba⁺⁺. The latter is practically insoluble in concentrated HNO₃.

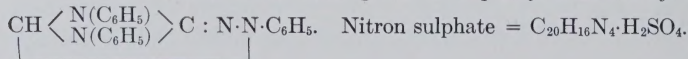
(a)-Group Reactions.

1-No precipitate, and no separation of crystals on standing, with AgNO₃, Ba(C₂H₃O₂)₂, Pb(C₂H₃O₂)₂, or Tl(C₂H₃O₂).

(b)-With Nitron.

Nitron sulphate¹ in acetic acid solution gives at once a heavy

¹ "Nitron" is the usual name given to Diphenylendanioldihydrotriazol



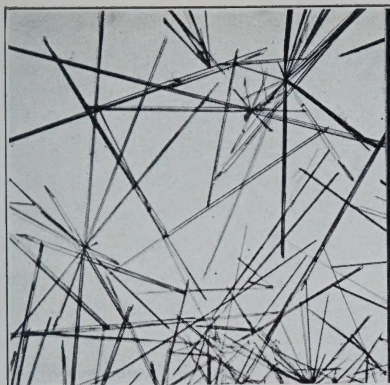


FIG. 150. CO_3^{2-} with Thallous Acetate. 50 $\times$.

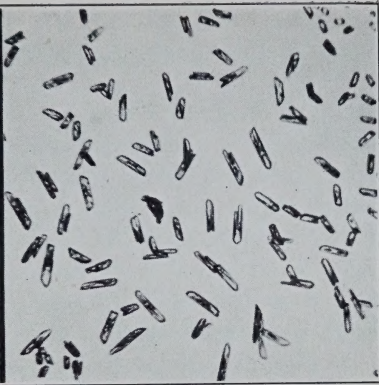


FIG. 151. CN^- with Silver Nitrate. 300 $\times$.

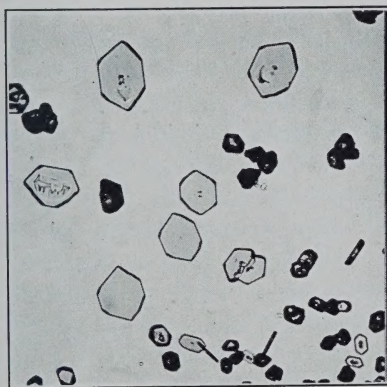


FIG. 152. Fe(CN)_6^{4-} with Thallous Acetate. 200 $\times$.

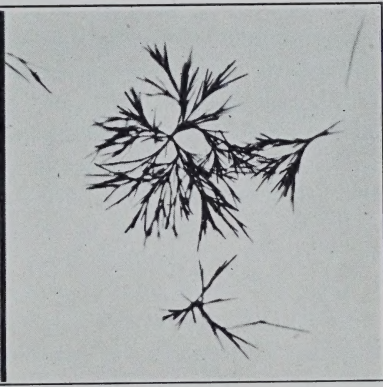


FIG. 153. SCN^- with Chlorauric Acid. 50 $\times$.

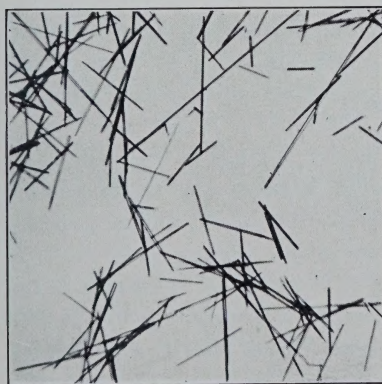


FIG. 154. NO_2^- with Silver Nitrate. 100 $\times$.



FIG. 155. NO_3^- with Nitron Sulphate. 100 $\times$.

white precipitate consisting of masses of exceedingly minute needles. In a few seconds sheaves of acicular prisms appear and later there are formed thin lath-like crystals or long thin prisms with square ends, giving polarization colors and parallel extinction (Fig. 155, page 299). Nitron nitrate has a very low solubility even in warm water, hence the reaction is a delicate one. The sheaves of white crystals, appearing brownish by reflected light, are characteristic.

In dilute solutions none of the salts of the common acids interfere save iodides and bichromates. With these salts there may be obtained crystals which closely resemble those of nitrate, but these crystals disappear upon even gentle warming; nitron nitrate will not.

From concentrated solutions there may be obtained under favorable conditions precipitates with nitrites, chlorates, perchlorates, phosphates, chromates, bichromates, iodides, ferro- and ferricyanides, oxalates and tartrates; but in no case, in dilute solutions with gentle warming, should there be any difficulty in differentiating between such precipitates and the crystals obtained with nitrates.

(c)-Reduction to NH_3 .

Nitrates are reduced to NH_3 by metallic aluminum in NaOH solution. The test is performed in the apparatus shown in Fig. 6, page 15. The solution to be tested is made strongly alkaline with NaOH and several small fragments of aluminum are introduced. The crucible is covered with an object slide carrying a hanging drop of H_2PtCl_6 and set aside for 30 minutes or more. If NH_3 has been formed characteristic crystals of $(\text{NH}_4)_2\text{PtCl}_6$ will be obtained. (See page 75.)

It is, of course, essential to perform a "blank" upon the reagents and also to test the "unknown" for NH_3 before the reduction with aluminum is attempted. If NH_3 is found in the "unknown" boil the solution with NaOH until all the NH_3 has been driven off.

Nitrites — NO_2^- . — Most simple nitrites are water-soluble, but many double and triple nitrites are difficultly soluble or almost insoluble.

The NO_2^- ion also enters into combinations with certain of the heavy metals to form complex ions, whose true nature is still uncertain and whose detection by ordinary qualitative methods is a matter of great difficulty.

(a)–Group Reactions.

1–With AgNO_3 there is obtained a felted mass of fine needles with long acicular prisms at the outer edge of the mass; on standing, short stout prisms with imperfectly developed ends are formed (Fig. 154, page 299). These crystals are colorless under the microscope and do not show their greenish tint unless viewed in masses by reflected light.

2–With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ or BaCl_2 no separation of crystals is obtained since $\text{Ba}(\text{NO}_2)_2$ is readily soluble.

(b)–Oxidizing Action.

Add to the drop to be tested a crystal of potassium iodide, then a little potato or canna starch and finally a trace of dilute acetic acid. The hydroiodic acid set free by the acid is oxidized by the nitrous acid; iodine is liberated and stains the starch blue or violet or black. This reaction is not specific as it is only the oxidizing power of NO_2^- which is tested.

Always test the potassium iodide, with starch and dilute sulphuric acid, so as to ascertain its purity and to be certain that no appreciable bluing of the starch takes place with the reagents alone.

(c)–Triple Nitrite.

To the drop of the solution to be tested add $\text{KC}_2\text{H}_3\text{O}_2$, and flow into the test drop thus prepared a drop of a solution of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ acidified with acetic acid. Minute crystals of potassium cobalt-nitrite are obtained. (See Cobalt, page 241.)

A variant of this test can be made by adapting the triple nitrite reaction to the detection of NO_2^- . (See page 186.) To the test drop add $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ and finally $\text{HC}_2\text{H}_3\text{O}_2$; tiny black cubes are obtained. (See Lead, page 184; Fig. 107, page 181.) The triple nitrite reaction is seldom applicable since with the introduction of both lead and copper there are likely to be many possible interferences.

Cyanates — CNO^- . — The cyanates of the alkalis are readily soluble in water; those of the alkaline earths are somewhat difficultly soluble. The cyanates of most of the remaining elements are insoluble, or only sparingly soluble.

(a)–Group Reactions.

1– AgNO_3 produces at once, even in very dilute solutions, a dense white “amorphous” precipitate. On standing a fringe of fine needles forms on the outer edge of the amorphous mass.

Toward the center of the dense precipitate the acicular crystals become short and more rod-like, but well-developed prisms are seldom obtained. Although AgCNO is slightly more soluble in hot than in cold water, flowing the warm reagent into a hot test drop, or attempting to recrystallize from hot water, does not give crystals sufficiently better formed to warrant the extra trouble.

2—The addition of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ causes the separation of colorless tiny disks, spherocrystals, and dumb-bell and hour-glass clusters of excessively fine needles. These crystal aggregates remain small; even on long standing a magnification of 150 to 200 $\times$ is required to disclose their habit.

3— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives an amorphous precipitate or one consisting of tiny disks somewhat irregular in outline.

4—No precipitate and no separation of crystals is obtained with $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$.

(b)—*Reaction with Hydroxylamine Hydrochloride and Ferric Chloride.*

To the moderately concentrated test drop acidified with HCl add a fragment of $\text{NH}_2\text{OH}\cdot\text{HCl}$ about the size of this (o). Stir until dissolved. Flow in by Method I a dilute solution of FeCl_3 . A purple-blue color results and an amorphous deep blue precipitate is formed.

The ferric chloride solution should be of such concentration that the drop on the object slide is just distinctly yellow when viewed over a white background.

The best results are obtained when the test drop is approximately neutral or very slightly acid with HCl .

CNO^- , if in alkaline solution, gives a precipitate of hydrous ferric oxide, and if then acidified with HCl , no visible reaction is obtained, but on long standing a precipitate of Prussian blue separates. CN^- gives the Prussian blue reaction at once, in acid solution.

Fossé² has shown that this test can be applied to a precipitate of AgCNO which has been obtained with AgNO_3 . The supernatant liquor is decanted and the precipitate washed thoroughly. A large fragment of hydroxylamine hydrochloride is added and the preparation stirred until the reagent is dissolved. A drop of FeCl_3 solution is added as above. A blue or violet color is produced.

Soluble alkali cyanates treated with FeCl_3 and then with dilute

² *Compt. rend.* **171**, 722 (1920).

HCl give a blue color and a blue precipitate of Prussian blue, but the color first formed when hydroxylamine is present is of a different hue and of greater intensity.

When the concentration of CNO^- ions in the test drop is high the purple or red-violet color first produced may change to a reddish brown and a brown precipitate may be formed. Under such conditions add to the center of the brown mass a tiny drop of dilute HCl. The hydrous oxide of iron is dissolved and a precipitate of Prussian blue is brought into evidence.

(c)—*Reaction with Cobalt Acetate.*

To the *concentrated* test drop add at its center a fragment of $\text{KC}_2\text{H}_3\text{O}_2$ and a *tiny* crystal of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$. The crystal will be surrounded immediately by a deep blue zone of color, in which floats a dark colored "amorphous" precipitate. As the reagent dissolves, the blue zone increases in diameter and eventually reaches the circumference of the drop. Allow the preparation to stand and spontaneously evaporate to dryness. Tablets, prisms, and large coarse dendrites of the deep blue ("cobalt blue") tetragonal salt $2\text{KCNO} \cdot \text{Co}(\text{CNO})_2$ are obtained. The test is successful only when CNO^- ions are in excess of Co^{++} and a double salt is possible. It is therefore imperative that the $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ be added with great caution, otherwise merely a fugitive blue color will be obtained and no blue salt will be found as the test drop passes to dryness.

The ion SCN^- also yields a blue color and a blue salt with cobalt acetate, but the hue of blue is very different and the dendrites of the cobalt thiocyanate salt have a different habit. A blue thiocyanate can be obtained only when the test drop consists of a practically saturated solution of an alkali thiocyanate.

Differentiation is simple if the blue color obtained with the unknown is compared with that given by drops prepared with KCNO and KSCN.

Another excellent method of distinguishing between the blue of CNO^- and that of SCN^- is to add a small drop of isoamyl alcohol to the preparation before it passes to dryness, stirring so as to bring the drop of the alcohol into intimate contact with all parts of the test drop. The blue cobalt cyanate salt is insoluble in the alcohol, but the thiocyanate salt is readily soluble, and in the latter case the drop of isoamylalcohol turns deep blue.³

³ Fossé: *Compt. rend.* **171**, 722 (1920).

Alkali cyanides yield no blue compound. If the cyanate contains even a small amount of cyanide the formation of the blue zone is prevented, and as the fragment of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ dissolves it will be surrounded by a yellow or brown zone.

(d)—*Detection of CNO^- based upon its decomposition products, CO_2 and NH_3 .*

When an alkali cyanate is heated with dilute H_2SO_4 , CO_2 is given off and $(\text{NH}_4)_2\text{SO}_4$ is formed in the solution.

Place the material in the crucible of the distilling apparatus (Fig. 6, page 15), proceeding as described on page 40. Add two or three drops of dilute H_2SO_4 , cover with an object slide carrying a hanging drop of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Warm gently. Remove the slide and examine the drop for crystals of lead carbonate. Evaporate the solution almost to dryness in the crucible, cool, add NaOH , and cover with a slide having a hanging drop of H_2PtCl_6 . Search for crystals of $(\text{NH}_4)_2\text{PtCl}_6$.

A "blank" must be made upon unknown and reagents to insure the absence of NH_3 .

If the unknown contains NH_4CNO it is obvious that the test for NH_3 production can give no evidence of the presence of CNO^- ions.

Cyanides — CN^- . — The alkali salts of the ion CN^- are very readily soluble in water, as are also the calcium and the strontium salts, but the barium salt is only slightly soluble. The cyanides formed by the remaining common elements are practically insoluble with the exception of HgCN which is slightly soluble.

However, many of these insoluble cyanides unite with the cyanides of the alkalis to form double salts which are readily soluble in water.

An aqueous solution can therefore contain both simple and double cyanides and also a number of complex cyanides.

Cyanogen enters into combinations to form a third class of compounds in which it constitutes a part of a complex ion — as for example, in $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$, the anions in these cases being the complexes $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$. Besides ferrous and ferric iron in these complexes we also find salts of $\text{Mn}(\text{CN})_6^{4-}$, $\text{Cr}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$; other complex ions are formed with members of the platinum group. Some of

the salts of these complex anions are water-soluble, some are insoluble.

The simple cyanides and double cyanides are readily transformed by acids into salts of the acid used and HCN is set free. But in the case of the complexes the addition of the acid has no appreciable effect, save that in certain complexes boiling with strong acids in concentrated solution may bring about a decomposition of the complex with the liberation of part if not all the cyanogen as HCN.

In these complex ions neither the metal nor the cyanogen responds to identity tests for the simple cations or anions corresponding to them unless the complex is broken down.

(a)-Group Reactions.

1-AgNO₃ gives a heavy white curdy precipitate. In very dilute solutions exceedingly minute prismatic crystals are obtained providing an *excess* of AgNO₃ is used. AgCN forms a number of water-soluble double cyanides; a precipitate first formed may therefore redissolve.

2-Ba(C₂H₃O₂)₂ added to solutions containing alkali cyanides gives a turbidity or precipitate consisting of tiny colorless dendritic aggregates, resembling clumps of moss.

(b)-Detection by Evolution of HCN.

For this purpose we can use the distilling crucible, proceeding as outlined on page 40. The material in question is moistened with several drops of dilute H₂SO₄ and covered with an object slide carrying a hanging drop of AgNO₃. Warm very gently and set aside for a few minutes. The drop of AgNO₃ is then searched for crystals of AgCN. These are very tiny highly refractive short stout prisms or rods, or sheaves of very slender needles (Fig. 151, page 299). A magnification of 150 to 200× is required for their resolution.

If no precipitate, turbidity, or cloudiness is formed in the drop of AgNO₃ it is safe to conclude that no HCN has been formed by the action of the H₂SO₄. The formation of AgCN cannot be taken as proof of the presence of CN⁻ ions, for the H₂SO₄ may have caused the liberation of HCN by decomposition of certain complex ions such as FeCN₆-----, etc. If, therefore, crystals of AgCN have been found, the experiment is repeated, using this time HNaCO₃ instead of H₂SO₄. Under these conditions crystals of AgCN will be formed from CN⁻ liberated from easily decomposable

cyanides, but not from the more stable complex ions, nor from stable cyanides not decomposable by HNaCO_3 .

Instead of AgNO_3 in the hanging drop, a drop of $(\text{NH}_4)_2\text{S}$ can be used to absorb the HCN set free. Careful evaporation of the reagent drop to dryness will give NH_4SCN which can be tested for by FeCl_3 (formation of blood red $\text{Fe}(\text{SCN})_3$).

Or the absorption can be made in a drop of a solution of sodium picrate with the production of a deep red color (picro-cyanate, $\text{NaC}_8\text{H}_4\text{N}_5\text{O}_6$). This reaction is of value when thus performed, but is not specific for CN^- if the reagent is applied directly to test drops, for a number of reducing substances give a red color with picric acid or sodium picrate.

Thiocyanates (SCN^-).—The thiocyanates of the alkalis, alkaline earths and Fe^{+++} are readily soluble in water. Those of Mn^{++} , Zn^{++} , Co^{++} are also water-soluble but less readily; those of Cu^{++} and Hg^{++} are sparingly soluble; those of the other metals are insoluble or difficultly soluble.

Many double and triple thiocyanates are formed having variable solubilities in water; in some cases the double salts are more soluble than either of the combining simple thiocyanates; in other cases the double thiocyanates are less soluble.

(a)–Group Reactions.

1– AgNO_3 produces an instantaneous heavy white curdy precipitate, insoluble in excess of thiocyanate and insoluble in dilute HNO_3 .

2–With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ no precipitate and no separation of crystals is obtained.

3–With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ there is no apparent reaction.

4– $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a precipitate in which no evidence of crystals can be detected, but merely a granular or sandy appearance with no change on standing.

5– $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ produces at once a mass of fine needles and irregular acicular dendrites. On standing, elongated, symmetrical, six-sided plates and tablets are formed, also long thin plates with oblique ends. Hexagonal skeletons are also abundant, and imperfectly developed plates and prisms. These crystals are strongly birefringent, and exhibit very brilliant polarization colors.

6–To the test drop add a very little HgCl_2 ; stir until dissolved, then flow in by Method I a dilute solution of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$. In

the presence of SCN^- the double thiocyanate of Hg^{++} and Zn^{++} will be formed. (See pages 124–131, Fig. 76, page 125.) The addition of a trace of cobalt or of copper will color the crystals of the double salt, and thus increase the sensitivity of the reaction.

7—Flow into the test drop a very dilute solution of FeCl_3 . A blood-red or yellowish-red color results from the formation of soluble ferric thiocyanate.

Complex Cyanides. — Cyanogen enters into many combinations which function as complex ions. Some of these complicated compounds are of debatable structure and are especially prevalent in the eighth group of the periodic system. Of these complex ions $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ are the only ones which are commonly encountered in industrial analyses.

Ferrocyanides — $\text{Fe}(\text{CN})_6^{4-}$. — The alkali ferrocyanides are readily soluble in water and form easily crystallizable salts.

The ferrocyanides of the alkaline earths are also soluble in water but less readily than those of the alkalis. $\text{Mg}_2\text{Fe}(\text{CN})_6$ is also water-soluble.

With the alkali ferrocyanides, many other ferrocyanides form double salts whose solubilities are different from those which might be expected. For example, the potassium calcium ferrocyanide is less soluble than calcium ferrocyanide, whereas the potassium barium ferrocyanide is more soluble than barium ferrocyanide. Analogous phenomena are to be met with in double salts of other elements.

The ferrocyanides of most of the elements other than the alkalis and alkaline earths form salts insoluble or difficultly soluble in water.

The great majority of ferrocyanides give almost colorless solutions in test drops, and small thin crystals, and most precipitates appear colorless or white. The most striking exceptions are those of iron, copper, and uranium.

(a)–Group Reactions.

1— AgNO_3 yields at once, even in very dilute solutions, a white heavy gelatinous precipitate of uniform texture throughout. There is no perceptible change in the “amorphous” character of the precipitate as the test drop passes to dryness.

2-With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ no separation of crystals of $\text{Ba}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ takes place unless the test drop is very concentrated. (See Barium, page 116.) If the concentration is sufficiently high, or the drop passes to dryness, colorless, weakly birefringent monoclinic, nearly rectangular tablets are obtained (Fig. 55, page 97). With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ there is obtained, on standing for some seconds, a fine granular precipitate which slowly changes into very minute square and rectangular plates and tablets (Fig. 54, page 97).

3- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates in very dilute solutions a white granular salt, which soon becomes distinctly crystalline. The tiny crystals present a great variety of shapes; there are irregular, rounded and angular grains, dendritic aggregates, tiny rods and rectangular prisms, some exhibiting parallel and some oblique extinction. All are strongly birefringent.

4-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ there is first obtained a white or colorless precipitate of tiny crystalline very irregular grains; these develop into elongated, somewhat dendritic six-sided plates, and thin plates in the form of regular hexagons. The plates are highly refractive, strongly birefringent, and exhibit brilliant polarization colors.

(b)-*Prussian Blue.*

$\text{Fe}(\text{CN})_6^{4-}$ gives a dark blue flocculent precipitate with both Fe^{++} and Fe^{+++} , insoluble in HCl . With Cu^{++} a chocolate brown curdy or flocculent precipitate is obtained.

(c)-Benzidine hydrochloride, added by Method I, does *not* give a blue oxidation product (distinction from $\text{Fe}(\text{CN})_6^{3-}$), for $\text{Fe}(\text{CN})_6^{4-}$ acts as a reducing compound, the iron in the complex being in the ferrous condition.

(d)-*Reaction with Quinoline.*

Quinoline hydrochloride gives rise to the formation of a difficultly soluble double quinoline ferrocyanide, separating in brownish-yellow or brown, strongly birefringent, tablets and thin plates. A few tablets elongate and become prismatic. The tablets are almost square or rectangular in outline, but many rhombiform tablets and grains are to be found with very acute angles. The crystals are dichroic and exhibit oblique extinction.

A moderate concentration of the test drop yields the best results. Free acids must be absent; their deleterious action can be mitigated by adding an alkali acetate.

Ferricyanides — $(\text{Fe}(\text{CN})_6)^{---}$. — The ferricyanides of the alkalis and alkaline earths are readily soluble in water. Many of the other elements give insoluble or sparingly soluble salts, but under the normal conditions which obtain in microscopic qualitative analysis no precipitate is probable with Al^{+++} , Hg^{++} , Pb^{++} , Sb^{+++} , Sn^{++++} , Cr^{+++} , $(\text{UO}_2)^{++}$, Fe^{+++} .

The ferricyanides commonly met with are reddish in color and give reddish-colored solutions.

A number of salts of $\text{Fe}(\text{CN})_6^{---}$ are soluble in 95 per cent alcohol; the corresponding salts of $\text{Fe}(\text{CN})_6^{----}$ are not.

(a) — *Group Reactions.*

1—With AgNO_3 there is formed a heavy reddish-brown gelatinous precipitate, which undergoes no change in its physical appearance as the test drop passes to dryness.

2—With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ no precipitate is obtained, and no separation of crystals until the test drop has evaporated to dryness. In the crystalline mass which results, it is impracticable to identify crystals of $\text{Ba}_3[\text{Fe}(\text{CN})_6]_2$ which may have been formed.

3— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives results analogous in all respects to those obtained with $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$.

4—With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ no precipitate is obtained and on standing no crystals ordinarily separate; but as the test drop concentrates by spontaneous evaporation there appears around the circumference a crystalline crust in which can be seen yellow and reddish-brown dendrites. If these dendrites are crushed so as to “seed” the preparation, short stout bipyramidal prisms and irregular crystalline grains are obtained. These crystals of thallium ferricyanide are remarkably dichroic. If thin, the change is from yellow to reddish-brown, if thick, from reddish-brown to jet black. They are strongly birefringent and extinguish parallel to the direction of elongation.

When testing for $\text{Fe}(\text{CN})_6^{---}$ it is essential that the test drop, to which $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ has been added, shall be allowed to stand until it becomes almost supersaturated, and then seeded.

(b) — *Prussian Blue.*

$\text{Fe}(\text{CN})_6^{---}$ gives a dark blue precipitate (or solution) with ferrous salts *but not with ferric salts* (distinction from $\text{Fe}(\text{CN})_6^{----}$). With solutions containing Fe^{+++} no perceptible change in the test drop can be observed, unless both test drop and reagent are

concentrated; under these latter circumstances a brown color is developed.

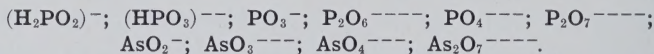
(c)–*Oxidizing Action.*

Benzidine hydrochloride⁴ added by Method I yields blue prisms, stars, and irregular dendrites and grains. This reaction is due to the oxidizing power of $\text{Fe}(\text{CN})_6^{--}$ and is not specific for this ion. Any mild oxidizing agent under similar conditions will give a similar reaction. Nevertheless the reaction is frequently useful in differentiating between ferro- and ferric-cyanides.

(d)–*Reaction with Quinoline.*

Quinoline hydrochloride added as in testing for $\text{Fe}(\text{CN})_6^{--}$ gives a bright yellow precipitate consisting of large prismatic dendrites. These crystals are rough and almost opaque at first, but some of them may become clear and transparent on standing. Many-faced lemon yellow tablets also appear after a short time; were it not for their color, these tablets might be confused with those given by $\text{Fe}(\text{CN})_6^{--}$. They are, however, less birefringent and are not noticeably dichroic. Extinction is oblique.

DETECTION OF THE ANIONS OF THE PHOSPHORUS GROUP



This great group includes ions of which many salts are not known, and many salts of debatable composition. Their properties and solubilities are exceedingly variable, and those which are unstable yield complicated decomposition products.

Most of these ions can be identified in the case of simple salts, but in mixture the problem becomes exceedingly difficult by qualitative methods alone.

The statements made below relative to solubilities are not accurate in all cases, but fit most commercial products. The data available in the literature are incomplete, and in many instances appear to have been obtained upon material of doubtful purity.

Because of the variable behavior of salts of these ions with different elements, the tests given below presuppose that a salt of sodium, of ammonium, or of potassium is to be tested. If a salt of some other element, it is assumed that transformation to an alkali salt is first practiced.

⁴ Behrens: *Zeit. anal. Chem.* **43**, 423 (1904).

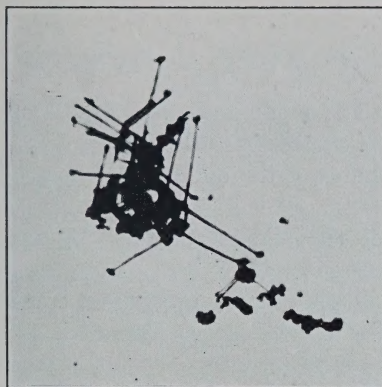


FIG. 156. AsO_4^{---} with Silver Nitrate. 500 $\times$.

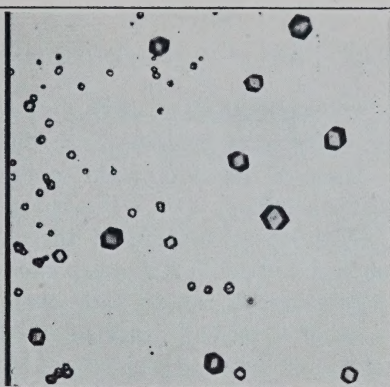


FIG. 157. AsO_4^{---} with Silver Nitrate. 500 $\times$.



FIG. 158. PO_4^{---} with Silver Nitrate. 200 $\times$.

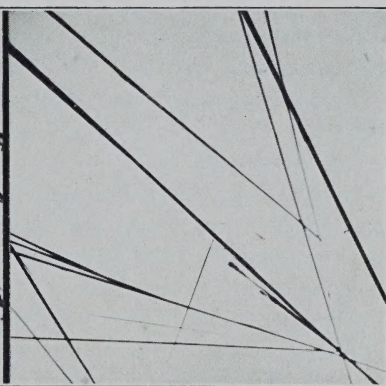


FIG. 159. PO_4^{---} with Thallous Acetate. 50 $\times$.



FIG. 160. HPO_3^{--} with Calcium Acetate. 150 $\times$.

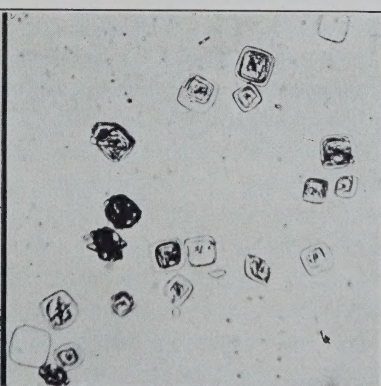


FIG. 161. HPO_3^{--} with Barium Acetate. 300 $\times$.

Orthophosphates — PO_4^{---} . — The mono-, di-, and tri-alkali phosphates are well known. All are soluble in cold water.

Some of the mono (acid) phosphates of the alkaline earths are water soluble.

With the exception of those of the alkalis substantially all normal and acid orthophosphates are insoluble.

Solutions of the di- and tri-alkali phosphates precipitate solutions of nearly all other salts. The precipitate consists of a di- or tri-metal orthophosphate or a basic phosphate.

All orthophosphates are dissolved or transposed by HNO_3 , HCl or H_2SO_4 . Nearly all are dissolved by $\text{HC}_2\text{H}_3\text{O}_2$; the common exceptions are Pb^{++} , Al^{+++} , Fe^{+++} . Nearly all are dissolved by H_3PO_4 ; the exceptions are Hg^{++} , Pb^{++} , Sn^{++} , Bi^{+++} .

Ammonium molybdate appears to be the most reliable agent for differentiating between the various acids of phosphorus, but soluble silicates, arsenates, tungstates, and vanadates must be absent.

(a)-Group Reactions.

1- AgNO_3 produces at once a heavy *light yellow* "amorphous" precipitate. (See Silver Group, page 290.) The precipitate soon becomes granular, and in a zone just beyond the precipitate, tiny yellow dendritic stars, crosses, radiates, and irregular clusters of fine needles are formed. Crystals which float are especially characteristic; most of them are three-branched (Fig. 158, page 311), more or less feathery or rough dendrites; the ends of each of the three branches are forked. As the concentration rises through spontaneous evaporation tiny highly refractive yellow crystalline triangular and tetrahedral grains separate around the circumference of the test drop.

2-With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ and with $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ a heavy white "amorphous" precipitate is obtained which may become granular on standing; but no recognizable crystals are formed.

3- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ throws down a heavy white curdy precipitate. On standing, very minute rods and needles appear. They occur singly in crosses, X's, and very small radiates. A magnification of about $300\times$ is required to reveal their form.

4-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ a very characteristic reaction is obtained. When the reagent is first added no result follows, but on standing very long colorless slender needles appear in large loose radiating clusters and in wisps. When the concentrations are favorable

the needles grow so long as to extend completely across the field of view. (See CO_3^{--} , page 298, Fig. 159, page 311, Fig. 150, page 299.)

(b)–*Reaction with “Magnesia Mixture.”*

In a drop of water dissolve a little $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$, add about twice as much NH_4Cl , stir and add a drop of NH_4OH . Into this reagent drop introduce a fragment of the material to be tested, and warm very gently. With orthophosphates $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ separates in large colorless feathery dendritic stars and skeletal crystals. See also Ammonium, page 77; Magnesium, page 121, Figs. 74, 75, page 113. $(\text{H}_2\text{PO}_2)^-$ gives no precipitate and no separation of crystals; $(\text{HPO}_3)^{--}$ yields tiny six-pointed stars and rosettes, curious dendrites reminding one of butterflies, and elongated plates with parallel sides and irregularly acute ends. PO_3^- gives an “amorphous” precipitate, then a few curious dendritic crystals. $\text{P}_2\text{O}_7^{----}$ yields a gelatinous precipitate only.

(c)–*Reaction with Ammonium Molybdate.*

Testing with ammonium molybdate requires that free HNO_3 shall always be present and also that the preparation shall be gently warmed. These two factors introduce a certain element of uncertainty in the results obtained, because warming with HNO_3 always converts some of the other phosphorus acids into orthophosphoric acid. It is therefore important to proceed as follows. The reagent drop is first prepared by adding a few fragments of $(\text{NH}_4)_5\text{H}_7(\text{MoO}_4)_6$ to a drop of water and adding thereto a small drop of dilute HNO_3 . Stir until all is dissolved. If a precipitate is formed add more HNO_3 . Place next to this reagent drop, a drop of a water solution of the material to be examined. Cause the reagent to flow into the test drop and warm *gently*. Cool and *examine at once*. PO_4^{---} gives immediately a yellow precipitate consisting of tiny highly refractive cubical or octahedral grains.

Since the conversion of $(\text{H}_2\text{PO}_2)^-$, $(\text{HPO}_3)^{--}$, $\text{P}_2\text{O}_7^{----}$ is always slow, ordinarily no yellow precipitate will be obtained save on standing, or if the heating has been prolonged, or at too high a temperature. By working *rapidly* there is little risk of confusing products of oxidation with PO_4^{---} originally present. The problem is not so simple when a small percentage of PO_4^{---} exists in salts other than orthophosphates, for it then becomes a question whether the PO_4^{---} has been produced by the action

of the HNO_3 . To solve such problems tests must be made for all of the phosphorus group ions, and from the data thus obtained a reliable decision can usually be reached.

Under the conditions given above for the performance of the test, metaphosphates — PO_3^- — appear to be far more rapidly converted into orthophosphates — PO_4^{---} — than the other salts listed in the preceding paragraph. Ammonium molybdate cannot therefore be depended upon to differentiate between PO_3^- and PO_4^{---} .

Arsenic, silicon, tungsten, and vanadium compounds interfere with the reaction.

Metaphosphates — PO_3^- . — All salts of the acid HPO_3 are insoluble or difficultly soluble in water. Even the sodium and potassium salts are difficultly soluble in cold water. NH_4PO_3 is practically insoluble. The alkali metaphosphates are more soluble in hot water; since, however, they are converted more or less rapidly into orthophosphates, when heated in solution, it is impracticable to heat solutions of unknown materials when a search must be made for anions of the phosphorus group.

(a) — Group Reactions.

1- AgNO_3 produces a white “amorphous” or somewhat granular precipitate. It is seldom that a test drop yields crystals of AgPO_3 . In rare cases tiny dendritic aggregates are obtained, in the form of lichen-like clumps, or rosettes of peculiar form. AgPO_3 is soluble in NH_4OH .

2-Neither $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ nor $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ yields results other than slight “amorphous” or granular precipitates.

(b)—To a drop of magnesia mixture (see PO_4^{---} , page 313) add a fragment of the material to be tested; warm *very gently*. An “amorphous” precipitate is obtained, with here and there a few curious dendrites of indescribable form, derived from fusiform rods or elliptical plates. These crystals are quite different from those obtained with PO_4^{---} .

Pyrophosphates — $\text{P}_2\text{O}_7^{----}$. — In the acid $\text{H}_4\text{P}_2\text{O}_7$ all four H atoms are replaceable. The salts formed are stable; those of the alkalis are soluble in water; those of the alkaline earths are difficultly soluble; most other pyrophosphates are insoluble.

$\text{P}_2\text{O}_7^{4-}$ fails to yield satisfactory crystals with the reagents usually employed.

With AgNO_3 a white gelatinous precipitate is obtained, becoming granular on standing and showing under a magnification of $300\times$ rod-like bodies and oval grains.

With barium, calcium, and lead acetates a gelatinous precipitate is obtained, in which no evidence of crystallization can be discovered with a magnification of $300\times$.

$\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$ gives no precipitate, but as the test drop passes to dryness, small disks, hexagonal plates, and rosettes are obtained.

Ammonium Molybdate gives no immediate precipitate, but on standing the HNO_3 converts the $\text{P}_2\text{O}_7^{4-}$ into PO_4^{3-} and a precipitate slowly develops.

In the absence of $(\text{MoO}_4^{2-})?$ and WO_4^{2-} , cobaltammine chloride (Luteo cobalt chloride, $\text{CoCl}_3(\text{NH}_3)_6$) affords an easy means of differentiating between pyrophosphates and other phosphates.⁵ In moderately concentrated solutions of alkali pyrophosphates this reagent gives first a heavy brownish precipitate, partly "amorphous" (?) and partly made up of an intricate mass of feathery dendritic sheaves, the individual components of which are drusy and curved. In a short time regular hexagons and skeletons of hexagons appear, mostly in the outer zone, and as the preparation concentrates, large numbers of hexagonal scales, plates, tablets, and rosettes are formed (Fig. 162, page 323). No similar reaction is obtained with $(\text{H}_2\text{PO}_2)^-$, $(\text{HPO}_3)^{2-}$, PO_3^- , $\text{P}_2\text{O}_6^{4-}$, PO_4^{3-} , AsO_3^- , AsO_3^{3-} , AsO_4^{3-} ; in solutions of salts of these ions no precipitate is formed, nor is there a separation of crystals until the test drop passes to dryness.

Both $(\text{MoO}_4^{2-})?$ and WO_4^{2-} give with cobaltammine chloride sheaves and radiates, and finally hexagonal scales, and plates, as the test drop goes to dryness; these crystals differ so little in appearance from those obtained with $\text{P}_2\text{O}_7^{4-}$ as to be practically indistinguishable. There is, nevertheless, little danger of error, for with $\text{P}_2\text{O}_7^{4-}$ the precipitation is instantaneous, while with $(\text{MoO}_4^{2-})?$ nothing is at first seen, and with WO_4^{2-} the first reaction is a mere turbidity.

Hypophosphates — $\text{P}_2\text{O}_6^{4-}$. — Comparatively little is known concerning these rare salts. They are quite stable and are not

⁵ Behrens-Kley: *op. cit.*, p. 139.

readily oxidized to phosphates by such energetic agents as Cl_2 , H_2CrO_4 or H_2O_2 .

The ion P_2O_6 is tetravalent; mono-, di-, tri-, and tetra-alkali salts are known. All are water-soluble. Most of the other elements form difficultly soluble salts with P_2O_6 ----

Since hypophosphates are not obtainable in commerce and are still of more theoretical than practical use, the detection of this ion need not be considered here.

Hypophosphites — $(\text{H}_2\text{PO}_2)^-$. — Hypophosphorus acid H_3PO_2 is a monobasic acid, only one of the hydrogen atoms being replaceable by a metal.

All the common cations appear to form hypophosphites except Sn^{++} , Cu^{++} , and Hg^+ ; those of Ag^+ and Fe^{+++} are very unstable.

The hypophosphites are very powerful reducing agents and if in a mixture may, when in solution, cause profound changes in the chemical nature of the substances present. In most cases the final product of the oxidation of $(\text{H}_2\text{PO}_2)^-$ is PO_4 ----. In many cases the reducing action is energetic in both acid and alkaline solutions, but in a few cases in acid solution only.

Most salts of $(\text{H}_2\text{PO}_2)^-$ when heated give off phosphine and hydrogen and are generally converted into meta- and pyrophosphates.

(a)–Group Reactions.

1–With AgNO_3 there is first formed a heavy white “amorphous” precipitate soon becoming granular. In the outer zone, tiny dendritic crystals appear as single rough rod-like bodies and radiates of short stout acicular crystals. Skeletal forms in X’s and H’s are also abundant. In a very short time the white mass becomes discolored and turns brown with a purple cast, due to the reduction of the AgNO_3 , and at the same time the tiny crystals disintegrate in large part. Minute oily droplets are formed, and collect in large drops at the circumference of the test drop.

2– $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives no precipitate, no separation of crystals, and no distinct crystals appear when the test drop passes to dryness.

3– $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives results similar to those obtained with $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$. (See (HPO_3) –.)

4– $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a white granular precipitate, changing in part into fusiform grains and very tiny short stout rods with

rounded ends. A magnification of 150 to 200 $\times$ is required for their resolution.

5—With $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)$ there is obtained a precipitate consisting of white (colorless) short stout rods with rounded ends, many cubical grains, and cubes in such a position as to appear to be hexagons. The rods are usually grouped in threes or sixes, and appear to be skeletons of octahedra.

Phosphites — $(\text{HPO}_3)^{--}$. — Phosphorous acid, H_3PO_3 , acts as a dibasic acid toward metallic cations. Both acid and “normal” salts are formed, but the third hydrogen atom cannot be replaced save by organic radicals.

Phosphites of the alkali metals are water-soluble; most other phosphites are insoluble in water, but soluble in H_3PO_3 , and are transposed by most acids.

The calcium, strontium, and barium salts of $(\text{HPO}_3)^{--}$ are difficultly soluble, thus affording a differentiation from the ready solubility of the hypophosphites of these elements.

The phosphites are strong reducing compounds and eventually change to phosphates in the presence of air.

(a)–Group Reactions.

1—With AgNO_3 a white “amorphous” or granular precipitate is at once produced, which rapidly becomes brown or black. The change appears to be even more rapid than in the case of $(\text{H}_2\text{PO}_2)^-$.

The granular precipitate develops in part, along the outer zone, into thin skeleton crystals in the form of distorted X’s in which the arms are more or less completely filled out, so that the crystal has the appearance of an envelope somewhat askew. Irregular dendritic forms float about.

At first sight the crystals appear to be similar to those obtained with $(\text{H}_2\text{PO}_2)^-$, but a closer study will reveal that they are recognizably different. The short stout rods of the silver salt of $(\text{H}_2\text{PO}_2)^{--}$ are absent, as are also the radiates. The oily droplets are also absent.

2—When $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ is added there is formed first a mere turbidity, but in a few seconds a heavy white (colorless) precipitate is thrown down, consisting of minute crystalline grains; these soon grow into thin disks of variable outline. The majority are oval or somewhat lenticular; others are almost square with well-rounded corners, and still others rhomb-shaped with rounded

angles. The little disks have a very characteristic appearance, and are not easily confused with the salts of other ions formed with $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ (Fig. 161, page 311).

$3\text{-Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ forms at once thin disks and exceedingly fine colorless needles grouped in irregular bundles, sheaves, and moss-like clumps. Soon around these aggregates, thin plates and scales are formed, so thin and with a refraction so nearly that of the mother liquor as to be almost invisible. As these platelets grow the aggregates develop into many-petaled flower-like clusters with imbricated obtuse or lanceolate petals. These crystal aggregates are very characteristic and appear to be specific for $(\text{HPO}_3)^--$ (Fig. 160, page 311).

$4\text{-Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields an immediate dense precipitate, consisting of tiny crystalline grains and small dendritic crystals of irregular shape. The reaction is of no specific value for the identification of $(\text{HPO}_3)^--$, since the crystals are too small and too irregular in form. Although they are unquestionably different in appearance from the lead salt of $(\text{H}_2\text{PO}_2)^-$, they are not sufficiently well developed to afford a safe differentiation.

$5\text{-Tl}(\text{C}_2\text{H}_3\text{O}_2)$ gives no precipitate, and no crystals separate on standing. Distinction from $(\text{H}_2\text{PO}_2)^-$.

Arsenates — AsO_4^{---} . — Orthoarsenic acid gives rise to salts containing the anion AsO_4^{---} . With monovalent elements mono-, di-, and tri-metal salts may be successively formed, but with the elements of higher valencies the nature of the salts depends upon variables, a discussion of which space will not permit.

Most orthoarsenates are isomorphous with the corresponding orthophosphates.

Although meta- and pyro-arsenic acids have been prepared, the evidence now available appears to indicate that salts of these two acids do not exist in aqueous solutions for any length of time, but become transformed into orthoarsenates.

The alkali orthoarsenates are soluble in water, most of them forming well-crystallizable salts; but the ortho-arsenates of the majority of the other elements are either insoluble or soluble with difficulty. However, it must not be overlooked that many of these insoluble arsenates can unite with alkali arsenates to form water-soluble double salts.

(a)-Group Reactions.

1-With AgNO_3 an immediate dark red granular precipitate is formed, which develops at once into irregular crystalline grains, most of which eventually change into three-armed skeletons and into three-, four-, and six-sided plates and tablets which are isotropic (Fig. 157, page 311). On standing these plates and tablets thicken and become deep garnet in color. Later bristling hairs may appear in grouped three-armed radiates, the arms of which form 120° angles with each other (Fig. 156, page 311). These radiates are very characteristic of silver arsenate. Skeletons of "octahedra" are sometimes formed. To obtain a suitable development of the granular precipitate it is necessary to tip the slide so as to cause the reagent to flow freely but slowly into the test drop.

If a dark red "amorphous" or very finely granular precipitate persists, without developing into crystals of definite shape and color, it is wise to repeat the test using ammoniacal silver nitrate as reagent; under these conditions well-formed crystals can almost invariably be formed, though they remain small.

Ag_3AsO_4 can be recrystallized from NH_4OH or HNO_3 . (See Silver, page 254; Arsenic, page 202.)

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a slight white "amorphous" precipitate in concentrated solutions, with no further change until the test drop is about to pass to dryness, when curious dendritic masses of fibrous crystals appear, some resembling lichens and liverworts, or flowers with thin lanceolate petals and compact fibrous centers.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives merely a faint "amorphous" precipitate which undergoes no change on standing; but in ammoniacal solutions large skeletal crystals are formed (Fig. 71, page 113).

4-With $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ a very heavy white gelatinous precipitate is obtained, with no change on standing other than a tendency to granulate, but the granulation is not marked.

5- $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ reacts with AsO_4^{---} in a manner analogous to its behavior with PO_4^{---} . Very long needles are formed, extending completely across the field. They unite in wisps and radiates but most of the needles occur singly. They are thicker and rougher than those obtained with PO_4^{---} , but the differences are too slight to afford a means of differentiating between the two salts. Between crossed nicols they are strongly birefringent and

mottled with small patches of polarization colors. (See CO_3 ,-- page 298.)

(b)—*Magnesia Mixture* (See PO_4 ---, page 313) gives a precipitate of $\text{NH}_4\text{MgAsO}_4 \cdot 6 \text{H}_2\text{O}$, identical in appearance with $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ and isomorphous with it. Arsenites do not give this reaction. Figs. 74, 75, page 113.

(c)—*Ammonium molybdate* produces a yellow precipitate of ammonium arsenomolybdate, which cannot be distinguished from the corresponding PO_4 --- compound. (See PO_4 ---, page 313.)

Arsenites— AsO_2^- ; $(\text{HASO}_3)^--$; $(\text{AsO}_3)^---$ or $(\text{As}_2\text{O}_6)^-----$.

— The alkali “arsenites” of commerce have the formula $R^+ \text{AsO}_2^-$ and are properly metarsenites. Alkali salts of the dibasic acid $\text{H}_2(\text{HASO}_3)$ are also possible. Both types of alkali “arsenites” are readily soluble in water.

All other elements apparently form “arsenites” derived from the acid $\text{H}_6\text{As}_2\text{O}_6$ or H_3AsO_3 , the number of hydrogen atoms replaced depending upon a number of variable conditions. These “arsenites,” known as orthoarsenites, are insoluble in water or soluble with difficulty, except that the arsenites of the alkaline earths are appreciably water-soluble. Many of the insoluble arsenites, however, can unite with the arsenites of the alkalis to form water-soluble double arsenites.

(a)—*Group Reactions.*

1— AgNO_3 gives first a white, then a heavy yellow gelatinous precipitate. Within the central open space in the advancing zone of precipitate small yellow granular disks and lenticular grains are formed. Many of these disks appear to be spherulites, but do not show a black cross between crossed nicols.

Many arsenites give, in addition to a yellow gelatinous precipitate, a few dark red crystalline grains, evidence of the presence of arsenates.

Because of the mixed nature of the yellowish-white precipitate it is best to test with ammoniacal silver nitrate; with this reagent arsenites give at once a clear bright yellow crystalline precipitate consisting of short rods with rounded ends, singly and in masses and radiates. The majority of crystals consist of elongated plates with parallel sides and notched ends. As the test drop evaporates, acicular crystals and dendritic groups are formed.

2—Barium arsenite is very soluble under the conditions govern-

ing its formation in the test drop, and no precipitate and no separation of crystals can be obtained.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, like $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, gives no precipitate and no separation of crystals.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a heavy white gelatinous precipitate only.

5- $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ yields tiny granular disks. These disks occur singly and are seldom united.

DETECTION OF THE ANIONS OF THE SULPHUR GROUP

SO_4^{--} ; SO_3^{--} ; $\text{S}_2\text{O}_3^{--}$; $\text{S}_2\text{O}_8^{--}$; $\text{S}_2\text{O}_6^{--}$; SeO_4^{--} ; S^{--}

Of these ions SO_4^{--} is of greatest importance because of the vast number of simple and double salts that are known and are common articles of commerce. Sulphites and sulphides rank next in importance and in numbers; of the salts of the remaining ions $\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are probably the only ones likely to be met with frequently in ordinary commercial products.

Salts of SO_4^{--} are seldom contaminated with salts of the other ions of the group, but the salts of the remaining ions ordinarily contain more or less impurities, such as sulphates or salts of the other more closely related ions, the nature of which depends upon the method used for the formation of the ion in question. These foreign ions, which are almost invariably present, introduce a complication in the analysis of very small amounts of material, and may trouble the analyst.

Most salts of the thionic acids ($\text{S}_2\text{O}_6^{--}$, $\text{S}_3\text{O}_6^{--}$, $\text{S}_4\text{O}_6^{--}$, $\text{S}_5\text{O}_6^{--}$, $\text{S}_6\text{O}_6^{--}$, $\text{S}_n\text{O}_6^{--}$) are unstable and rapidly decompose in aqueous solutions. Their detection and identification are therefore difficult and in most cases impossible; moreover, characteristic microscopic reactions worked out on materials of known purity are still lacking.

Sulphates — SO_4^{--} .

(a)-Group Reactions.

1-The precipitate with BaCl_2 or $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ is exceedingly fine (in "neutral" solutions) or at the most, finely granular, insoluble in water and not appreciably soluble in dilute HNO_3 .

2-Silver nitrate produces no precipitate in *dilute* test drops, but from concentrated solution, colorless, highly refractive rhomb-shaped tablets, and short stout prisms with angular ends of

pseudo-octahedra separate. The crystals of Ag_2SO_4 have a characteristic habit and are easily recognized. If either CrO_4^{--} or $\text{Cr}_2\text{O}_7^{--}$ is present in small amount the Ag_2SO_4 crystals are colored yellow to red and are pleochroic (isomorphous mixture). (Fig. 163, page 323. In the photograph, the black "prisms" are tablets seen edgewise.)

3-With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ by Method I, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is obtained in characteristic needles, sheaves, radiates, arrow-head twins, or masses of broad foliated plates. (See Calcium, page 96.) The crystals are soluble in water and are therefore obtainable only when the test drop contains a fairly high concentration of SO_4^{--} . Ions giving insoluble compounds with calcium either mask this reaction or interfere with it to the extent of preventing the separation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; in such cases the addition of a *very little* HNO_3 to the test drop after the $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, and gentle warming, may give rise to conditions more favorable for the separation of the gypsum crystals; the latter are, however, quite soluble in HNO_3 , so that too much acid will result in failure to detect SO_4^{--} even when present in relatively large amount (Figs. 56, 57, page 97).

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is soluble in alkali thiosulphates; hence in mixtures containing SO_4^{--} and $\text{S}_2\text{O}_3^{---}$ no crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ may appear until the test drop passes almost to dryness, and the separation of various other salts may completely mask the reaction.

4-With $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ there is instantly formed a heavy dense white finely granular precipitate, practically insoluble in water and very difficultly soluble in HNO_3 .

On standing for a short time the granular precipitate changes into tiny bristling dendritic grains and irregular masses of short stout sharply angular crystals.

5-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ by Method I, Tl_2SO_4 is obtained in colorless long thin highly refractive rhombs and orthorhombic prisms with oblique or angular ends (Fig. 165, page 323). These plate-like prisms soon build up to thick well-formed rectangular tablets and prisms with pyramidal or obliquely truncated ends; irregular tablets are also formed (Fig. 164, page 323).

When using $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ as a reagent it is especially important to perform several tests, using test drops of varying concentrations.

(b)-The addition of dilute H_2SO_4 sets free no SO_2 .

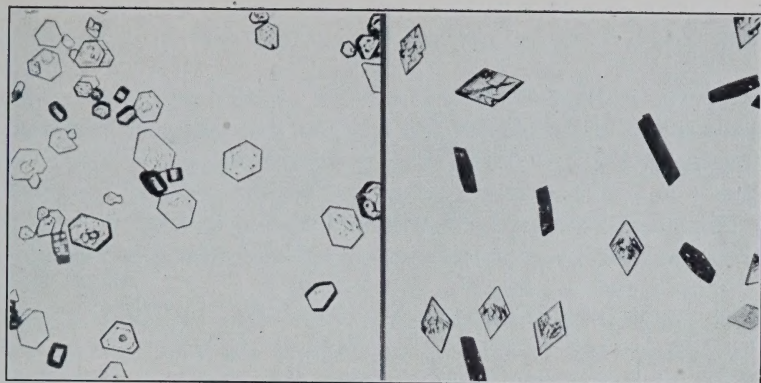


FIG. 162. $P_2O_7^{4-}$ with Luteocobalt Chloride. 200X.

FIG. 163. SO_4^{2-} with Silver Nitrate. 100X.

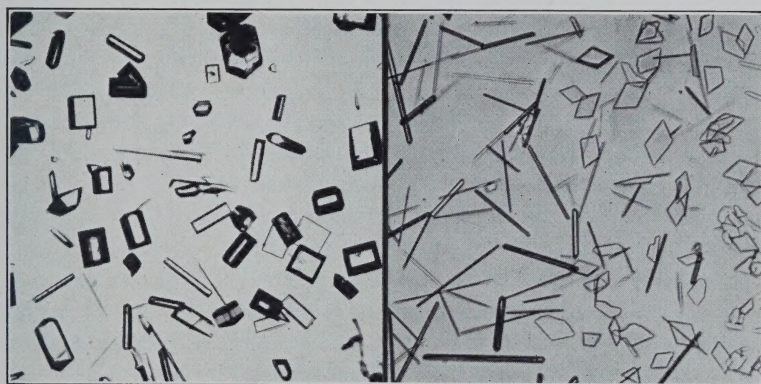


FIG. 164. SO_4^{2-} with Thallous Acetate. 200X.

FIG. 165. SO_4^{2-} with Thallous Acetate. 200X.

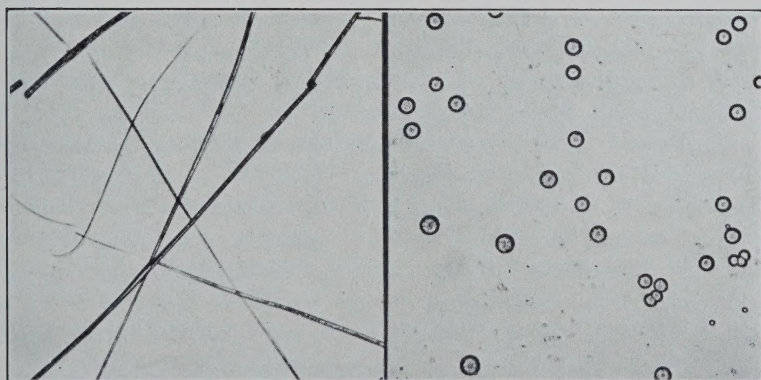


FIG. 166. SeO_4^{2-} with Thallous Acetate. 200X.

FIG. 167. SO_3^{2-} with Calcium Acetate. 200X.

(c)–The addition of dilute H_2SO_4 and metallic zinc produces no more H_2S than a “blank” test made at the same time with zinc and H_2SO_4 alone.

Sulphites — SO_3^{--} . — The normal and acid sulphites of the alkalis are readily soluble in water, but the normal sulphites of all other metals are insoluble or nearly so.

The sulphites of the alkaline earths and a few metallic sulphites dissolve in water containing SO_2 , forming soluble acid sulphites (bisulphites). When solutions of these “bisulphites” are boiled, the normal sulphite is reprecipitated. Boiling does not cause a decomposition of alkali sulphites.

SO_3^{--} in an insoluble sulphite can be converted into water-soluble Na_2SO_3 by boiling with a concentrated solution of Na_2CO_3 ; or SO_2 can be liberated by an acid and identified.

SO_3^{--} is readily oxidized to SO_4^{--} by concentrated HNO_3 , strong bromine water, or Na_2O_2 . After the excess of the oxidizing agent has been removed by boiling, SO_4^{--} can be tested for by $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. (See page 96.) Conversion to SO_4^{--} by these reactions is not confined to SO_3^{--} , but is common to practically all the other sulphur acids.

Sulphites in solution reduce HIO_3 , iodine being set free, which will color starch granules blue. SO_2 liberated by an acid and expelled by Method IX, page 40, will also give the blue color with HIO_3 and starch, or KI and starch. This reaction is not specific for SO_3^{--} .

(a)–Group Reactions.

1– AgNO_3 added by Method I gives an immediate snow-white “amorphous” or granular precipitate of Ag_2SO_3 , changing rapidly to brown on boiling, metallic silver and H_2SO_4 being formed. The white Ag_2SO_3 is readily soluble in HNO_3 and is also soluble in excess of alkali sulphites.

Since most sulphites contain sulphates, Ag_2SO_4 separates in characteristic crystals on standing. (See SO_4^{--} , page 321, Fig. 163, page 323.) The appearance of Ag_2SO_4 crystals in very small amount cannot be taken as proof of the presence of sulphates in the sulphite under examination, for when using AgNO_3 as reagent there appears to be always an oxidation of some SO_3^{--} to SO_4^{--} .

2–With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ or BaCl_2 a heavy white granular precipitate is first formed. On standing tiny dendritic crystals appear in a

zone just at the edge of the mass of precipitate. Eventually these crystals grow slightly larger and rhomboidal skeleton plates can be readily resolved under a magnification of 150 to 200 $\times$. BaSO_3 can be distinguished from BaSO_4 by adding HCl , in which BaSO_3 is readily soluble but BaSO_4 is practically insoluble.

The tiny crystals of BaSO_3 are anisotropic but are only weakly birefringent.

3—The addition of $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ by Method I gives rise to the formation of strongly birefringent tiny disks and spherulites; the latter develop into botryoidal grains or aggregates (Fig. 167, page 323). The separation is slow and the grains always remain small. This reaction offers a simple means of distinguishing between SO_3^{--} and $\text{S}_2\text{O}_3^{--}$, for the calcium salt of S_2O_3 is too soluble to separate under the conditions which obtain. After allowing sufficient time for the separation of the sulphite crystals, the supernatant solution can be decanted and tested for S_2O_3 by means of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. (See page 328.)

4—In moderately concentrated solutions $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$ forms long dendritic needles built up of angular grains. These acicular dendrites occur singly, in irregular clusters, or in skeleton crystals in the form of X's or H's with stout rough arms usually straight but occasionally curved. At the circumference of the test drop the dendrites are usually curved in a peculiar fashion. The majority of crystals that eventually separate are irregular grains with angles more or less rounded, most of them showing a derivation from the X- and H-form skeletons.

(b)—*Reduction to H_2S .*

SO_3^{--} is readily reduced to H_2S by metallic zinc and HCl . Test in the crucible using as reagent a hanging drop of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ made alkaline with NaOH ; the white precipitate turns black. Or absorb the H_2S in a hanging drop of NaOH and test with sodium nitroprusside; or expose a moistened crystal of AgNO_3 , or one of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, to the gas evolved.

Thiosulphates — $\text{S}_2\text{O}_3^{--}$. — Salts of this ion, properly termed thiosulphates, must not be confused with salts of the ion SO_2^{--} , hyposulphites (hydrosulphites), although the sodium salt $\text{Na}_2\text{S}_2\text{O}_3$ is still known to photographers as "hypo" — a designation retained from the days when the acid $\text{H}_2\text{S}_2\text{O}_3$ was commonly known as hyposulphurous acid.

Most thiosulphates are unstable, some of them decomposing almost as soon as formed. The usual types of decomposition are to sulphates and polysulphides, or to sulphur and H_2S . In the latter case there will generally result a sulphate, free sulphur, and the sulphide of the metal, but intermediate compounds are almost always formed also.

It is important that the analyst bear this instability in mind, for it is obvious that in but few cases will he have to deal with a thiosulphate entirely free from other sulphur acids.

Soluble and water-insoluble thiosulphates are decomposed by acids and dissolved, and sulphur is usually precipitated.

(a)-Group Reactions.

1-With AgNO_3 there is first formed a white, dense, granular precipitate. This rapidly turns yellow, then dark yellow, and finally brown or black, due to the formation of silver sulphide. Sulphur is usually set free.

SO_4^{--} ions are generally present in considerable amounts in commercial grades of thiosulphates; hence crystals of Ag_2SO_4 soon appear in the test drop. These crystals, though still preserving their characteristic habit, are discolored by Ag_2S and appear yellow, brown, or black. Careful observation will disclose that these crystals are "stained" on the outside and are not the result of the separation of crystals of salts containing a cation giving rise to a colored compound. It is important that the preparation be allowed to stand for a short time until the yellow hue changes to brown or black, otherwise the analyst may form the hasty conclusion that CrO_4^{--} ions are also present, since certain yellow hues resemble somewhat those imparted by a very little CrO_4^{--} .

$\text{Ag}_2\text{S}_2\text{O}_3$ is readily soluble in excess of alkali sulphate, because of the formation of the double salt $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3$. Hence it is important that the AgNO_3 reagent drop shall be concentrated, and that sufficient solution shall have been led into the test drop to insure a permanent precipitate.

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ forms $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$, a white, finely granular precipitate, only slightly soluble in water, but readily soluble in acids.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ causes no precipitate in solutions of thiosulphates — a distinction from sulphites. In a mixture of SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ the SO_3^{--} can be precipitated with $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ and

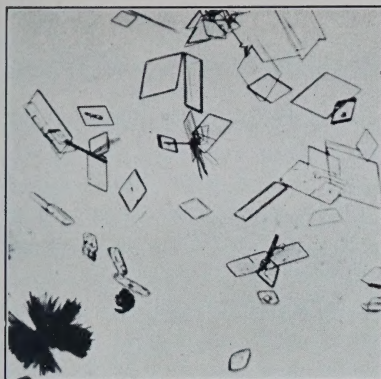


FIG. 168. $\text{S}_2\text{O}_3^{--}$ with Lead Acetate. 150 $\times$.



FIG. 169. $\text{S}_2\text{O}_3^{--}$ with Lead Acetate. 150 $\times$.

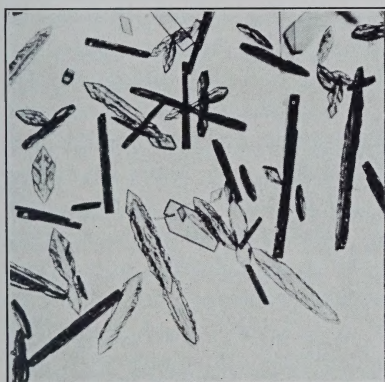


FIG. 170. CrO_4^{--} with Silver Nitrate. 100 $\times$.

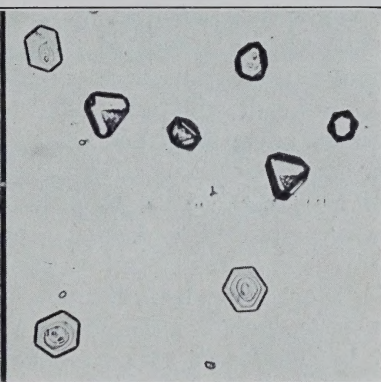


FIG. 171. Cl^- with Silver Nitrate and the AgCl recrystallized from NH_4OH . 500 $\times$.

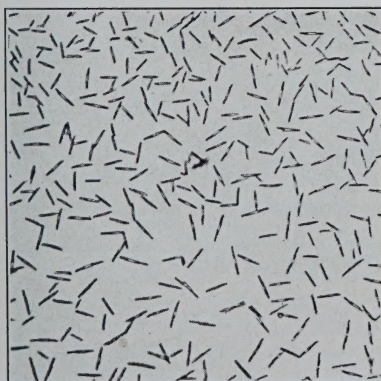


FIG. 172. Br_2 (Br^- ; BrO_3^-) with Metaphenylenediamine Hydrochloride. 200 $\times$.

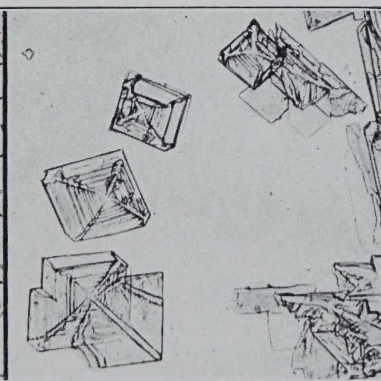


FIG. 173. $(\text{C}_2\text{H}_3\text{O}_2)^-$ with Mercurous Nitrate. 100 $\times$.

the clear solution tested for S_2O_3 after decantation, filtration, or separation by means of the centrifuge.

4—A concentrated solution of a salt of S_2O_3 treated with acetic acid gives a white precipitate of sulphur, and SO_2 is formed. The latter can be tested by KI and starch, either in the solution, or better, by expulsion by Method IX, page 40.

5—With metallic zinc and HCl , thiosulphates are reduced to H_2S . (See SO_3 , page 325.)

6—A reaction which appears to be constant and peculiar to $\text{S}_2\text{O}_3^{--}$ is that obtained when $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ is added to alkali thiosulphates by Method I. There is first obtained a dense white granular almost “amorphous” precipitate. After standing a few minutes thin, colorless, well-formed, highly refractive, lozenge-shaped plates in foliated aggregates separate within the granular mass of precipitate or in a zone just beyond it (Fig. 168, page 327). Arrow-head twins are frequent. These rhomboidal plates and tablets are strongly birefringent and exhibit brilliant polarization colors. This salt is soluble in excess of $\text{Na}_2\text{S}_2\text{O}_3$, hence an excess of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ must be present to insure its separation. This is accomplished by having a high concentration in the reagent drop, and taking steps to prevent the reagent drop from “breaking away” from the test drop — a tendency strongly marked when a concentrated solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ is used as the reagent.

In addition to the rhomb-shaped tablets and plates there are always formed disks and spherulites of exceedingly fine needles; these spherulites unite into dumb-bell shaped aggregates, which in turn develop into relatively large sheaves (Fig. 169, page 327). Save when in disk-form, these aggregates are remarkable for their light-scattering power, and by transmitted light appear to be perfectly opaque and therefore jet black. The disks are strongly birefringent and exhibit brilliant polarization colors.

SO_4^{--} ions interfere, probably because of the removal of Pb^{++} ; but if the reagent is properly applied and the SO_4^{--} ions are not greatly in excess of the $\text{S}_2\text{O}_3^{--}$ both types of crystals typical of $\text{S}_2\text{O}_3^{--}$ are obtained. If the $\text{S}_2\text{O}_3^{--}$ ions are present in very small amount the rhombs are not always formed, because it appears to be difficult to hit upon just the proper equilibrium conditions to bring about their formation.

In testing for $\text{S}_2\text{O}_3^{--}$ with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ it is more important than in most cases to experiment with test drops of several differ-

ent concentrations, and to allow the preparations to stand for several minutes and never to neglect to search the preparation using crossed nicols. In mixtures a dense granular precipitate may mask the rhombs, but between crossed nicols they are readily found because of their strong birefringence.

By means of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ it is possible to detect soluble $\text{S}_2\text{O}_8^{--}$ in the presence of soluble sulphites, persulphates, and thionates.

The authors have found that the addition of a *very little* $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ to a test drop containing a dense mass of precipitate sometimes improves the test, but if too much is added the test fails completely.

7—The addition of $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ gives rise to tiny white stars, crosses, X's, irregular crystalline grains, and peculiar feathery dendrites. These tiny skeletal and dendritic crystals are highly refractive and scatter light very strongly. Their birefringence is weak.

Polythionates also give skeletal and dendritic crystals with $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$, but these crystals grow much larger and have a very different appearance; moreover, long prisms with pyramidal ends are eventually formed. These prisms extinguish parallel with the direction of their elongation.

Persulphates — $\text{S}_2\text{O}_8^{--}$ (SO_4^{--}). — All salts of the ion $\text{S}_2\text{O}_8^{--}$ which are likely to be met with are soluble in cold water; the least soluble of them is $\text{K}_2\text{S}_2\text{O}_8$.

The persulphates are very strong oxidizing agents, converting manganese, cobalt, nickel, and lead salts into peroxides.

In the solid state the salts of $\text{S}_2\text{O}_8^{--}$ are quite stable. Most of them crystallize well.

In aqueous solution persulphates slowly decompose; usually oxygen is given off, a sulphate of the cation present is formed, and H_2SO_4 is set free. An exception to this reaction is to be found in the decomposition of aqueous solutions of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. It is mentioned here because it affords a striking illustration of the extraordinary oxidizing power of $\text{S}_2\text{O}_8^{--}$; in this case no oxygen is evolved but part of the NH_4 is oxidized to HNO_3 ; the final products of decomposition are $(\text{NH}_4)\text{HSO}_4$, free H_2SO_4 , and free HNO_3 .

No microscopic reactions constant and peculiar to $\text{S}_2\text{O}_8^{--}$ have

yet been found, and the identification of this ion must be largely through a process of elimination.

The reaction *a*-1 distinguishes $\text{S}_2\text{O}_8^{--}$ from SO_4^{--} but to obtain the formation of black (or brown) silver oxide the test drop must be concentrated with respect to salts of $\text{S}_2\text{O}_8^{--}$.

Reaction (*b*) will differentiate $\text{S}_2\text{O}_8^{--}$ and SO_4^{--} from all the other usual acids of sulphur.

(a)-Group Reactions.

1- AgNO_3 produces almost at once a heavy white crystalline precipitate. The crystals first formed closely resemble those of Ag_2SO_4 (which are always present) but are more elongated and slightly lenticular, that is, they have bulging sides midway their length; later rhombs and six-sided tablets abound, as also short stout prisms with angular ends; but since the resemblance to those of Ag_2SO_4 is so close it is impossible to decide whether the crystals obtained are those of a silver salt of $\text{S}_2\text{O}_8^{--}$ or of SO_4^{--} , the latter slightly modified by the presence of $\text{S}_2\text{O}_8^{--}$ ions.

In a short time a blackish cloud of Ag_2O appears and the crystals become stained black; black flocs float about in the liquid and tiny black disks deposit upon the object slide. Often, just as the test drop passes to dryness, a ring of brown appears at the circumference of the test drop. The phenomenon of blackening is very different from that obtained with $\text{S}_2\text{O}_3^{--}$ and the two cannot be confused; moreover, with $\text{S}_2\text{O}_8^{--}$ the silver salt does not at first turn yellow.

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ (or BaCl_2) forms a white, fine, granular precipitate, which rapidly develops into colorless irregularly angular grains having a more or less diamond-shaped outline. Short rods with rounded ends and rods with a central swelling are also abundant. These crystals are accompanied by finely granular BaSO_4 . When much decomposition of $\text{S}_2\text{O}_8^{--}$ has taken place, or if the persulphate contains much sulphate, the fine precipitate of BaSO_4 may mask the crystals of $\text{BaS}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$.

Since $\text{BaS}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ is moderately soluble, crystals of this salt will not separate unless the test drop is concentrated. In dilute solutions no immediate separation can occur, and only BaSO_4 is precipitated. The same difficulty is here encountered as in *a*-1 with the silver salts, for BaSO_4 may be precipitated in crystalline form; it is obvious that Ba^{++} does not differentiate between $\text{S}_2\text{O}_8^{--}$ and SO_4^{--} .

3-With $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ there is obtained a precipitate of white granular PbSO_4 , and beyond this crystalline grains and tiny rods are formed; the latter usually occur singly. On standing the crystalline grains increase slightly in size and assume an elliptical outline, or become distinct rhombs with their acute angles somewhat rounded. Here again the differentiation between $\text{S}_2\text{O}_8^{--}$ and SO_4^{--} is questionable.

4-With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ no precipitate is formed and there is no separation of crystals even in concentrated solutions, but on standing crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ appear in abundance. If the material being tested consists of a persulphate containing a large amount of preformed sulphate, gypsum crystals appear at once from concentrated solution, but this difference in the rate of separation of gypsum crystals is not a safe basis upon which to found an opinion relative to the purity of a given persulphate; nor is it possible to decide by calcium acetate alone whether the material in hand is a persulphate or a mixture of sulphates and persulphates.

5-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ no crystals other than Tl_2SO_4 appear to be formed. This accords with the results obtained by Foster and Smith,⁶ who found thallium persulphate so unstable as to decompose at once in air.

(b)- KMnO_4 added by Method I to *freshly prepared* solutions of persulphates is *not* decolorized nor changed in hue, whereas decolorization, with or without the precipitation of oxides of manganese, takes place at once in presence of SO_3^{--} , $\text{S}_2\text{O}_3^{--}$, S^{--} , and the thionate ions $\text{S}_2\text{O}_6^{--}$, $\text{S}_3\text{O}_6^{--}$, $\text{S}_4\text{O}_6^{--}$, $\text{S}_5\text{O}_6^{--}$.

Of the sulphur acids likely to be met with, the sulphates and persulphates alone do not decolorize KMnO_4 .

Sulphides — $\text{S}^{--}(\text{H}_2\text{S})$. — The sulphides of the alkalis and those of the alkaline earths are readily soluble in water, but in their aqueous solutions they are unstable and rapidly decompose; sulphur is set free, and complex thio-compounds are formed. Usually some S^{--} is oxidized to SO_4^{--} .

The sulphides of the heavy metals are insoluble in water. Most of them are stable in dry air, but in the presence of moisture or acids many of them are decomposed.

⁶ *Jour. Amer. Chem. Soc.* **21**, 934 (1899).

S⁻⁻ in insoluble sulphides is most satisfactorily detected by fusion:

(a)–With Na₂CO₃ and KNO₃ or KClO₃, whereby the S⁻⁻ is converted into SO₄⁻⁻. After the addition of HC₂H₃O₂ to decompose the excess of Na₂CO₃ the solution is tested for SO₄⁻⁻.

(b)–With KOH, and testing with sodium nitroprusside; or adding an acid, setting free H₂S and testing for this gas by the hanging-drop method using Pb(C₂H₃O₂)₂ and AgNO₃ solutions, or passing the gas over crystals of Pb(C₂H₃O₂)₂ and AgNO₃ in a capillary tube. (See page 42.)

S⁻⁻ in water-soluble sulphides gives a black precipitate with AgNO₃ in the Bunsen-Treadwell grouping, but no appreciable reaction with BaCl₂, other than in a few cases a faint cloudiness due to sulphur set free; slight decompositions of this character are seldom discernible in a test drop under the microscope.

Slow decompositions of H₂S solutions, and solutions of sulphides, or of thio-compounds, or reducing decompositions of SO₄⁻⁻ and of other sulphur-containing ions not infrequently give rise to a precipitate of crystalline sulphur. These crystals, if formed at ordinary temperatures, are faintly yellow, glistening, very highly refractive, very strongly birefringent, orthorhombic, bipyramidal grains with a melting point of 108° C. At 98° C. inversion to monoclinic sulphur takes place; above 98° monoclinic sulphur is stable and may persist in metastable form at lower temperatures. Tiny crystals of sulphur can be recognized by their color, high refraction and double refraction, melting point, flammability, burning with a blue flame, and giving fumes of SO₂. The crystals are brittle (hardness 2), and insoluble in water and weak acids; they are soluble in CS₂; fused with Na₂CO₃ and KNO₃ sulphates are obtained, and fused with KOH sulphides are formed.

Free sulphur and most sulphides can be converted into H₂SO₄ by repeated treatments with hot concentrated HNO₃. The treatment must be continued until a clear solution is obtained. In the case of free sulphur the crystalline form is much more resistant to oxidation than when “amorphous” or sublimed.

Oxidation can also be accomplished with bromine. With small amounts of material the oxidation is conveniently carried out in the distillation crucible. A few drops of very strong bromine water (or of bromine) are placed in the crucible and the moistened material is exposed in a hanging drop to the action of the vapors.

Gentle heating favors the reaction. Oxidations with HNO_3 and Br_2 should be performed in a hood.

Selenates — SeO_4^{--} . — Selenates are grouped here under the sulphur acids because of their close resemblance to sulphates and because of the large number of simple and double selenates that are known. Most of these selenates are isomorphous with the sulphates of the same metal.

The detection of SeO_4^{--} turns upon the identification of selenium in the compound (See Selenium, page 227) and upon observations of the close similarity in the behavior of SeO_4^{--} and SO_4^{--} to reagents. Although the common salts of SeO_4^{--} separate from test drops in crystal forms closely resembling each other, the experienced analyst can often distinguish slight differences in the character of the crystals sufficient to lead him to suspect the presence of selenates in the material he may have under examination; but it is usually necessary for him to test drops of varying concentration. In the outline given below these minor differences have been somewhat overemphasized.

(a)–Group Reactions.

1- AgNO_3 produces at once a very dense heavy white granular precipitate. In test drops of approximately like concentration of SeO_4^{--} and of SO_4^{--} the separation of Ag_2SeO_4 is more rapid and denser than that of Ag_2SO_4 .

The crystals of Ag_2SeO_4 do not develop into well-formed tablets, plates, and rhombs as readily as those of Ag_2SO_4 , but remain smaller, more irregular, and more dendritic. The rhombs usually “sprout” at the acute ends, becoming rough acicular dendrites with rhombiform central outline. They are highly refractive and scatter light more strongly than crystals of Ag_2SO_4 .

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a white granular precipitate somewhat less quickly formed than that with SO_4^{--} , but on the other hand readily developing into much larger crystalline grains. These grains are generally thicker than those formed by BaSO_4 , and have an hour-glass shape. Most of them are colorless; others are sufficiently drusy to scatter light and appear white, or, by transmitted light, black. Colorless lenticular grains also abound. The chief difference between BaSeO_4 and BaSO_4 as formed in test drops is that BaSeO_4 separates more slowly and forms larger and thicker crystalline grains.

3—With $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)$ no immediate separation of crystals occurs, but on standing long slender prisms appear and many extraordinarily fine hair-like crystals occur singly, rarely in groups or masses (Fig. 166, page 323). Although long, they are less prone to bend and curve than most trichiten crystals generally are. When the prisms grow thick they are not distinguishable from those of Ti_2SO_4 (Figs. 164, 165, page 323).

Ti_2SeO_4 crystals are characterized by their high refractive power and strong birefringence with parallel extinction. The great majority of the crystals are longer and slenderer than those of Ti_2SO_3 and have terminal angles less well developed.

4—With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ no distinct crystals are obtained even when the test drop goes to dryness; the dry film shows only irregular rosettes of very low refractive index, not differing materially from the crystals of the reagent.

5— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates at once, from even very dilute solutions, a snow-white, dense, "amorphous" mass, soon changing into very minute granular crystals, and eventually developing into crystalline grains and very short rods with rounded ends. The crystals always remain small, and require a magnification of about $200\times$ for their resolution.

Selenites — SeO_3^{--} . — The selenites are, for the most part, unstable salts corresponding to the sulphites. Although the probability of the analyst's having to test for the presence of selenites is very remote, a brief résumé of the group reactions of SeO_3^{--} is nevertheless given.

As in the case of selenates, the first step is the detection of selenium.

(a)–Group Reactions.

1— AgNO_3 gives in very dilute solutions a dense white precipitate consisting of tiny grains and short acicular crystals in crosses and irregular groups. On standing a short time these acicular crystals become rough and bristling, and develop into long dendrites with one end spreading out into thin leaf-like or fern-like masses. The body of these long dendrites bristles with tiny angular crystals, growing parallel with each other at very acute angles with the directions of elongation of the acicular dendrites.

2— $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives no reaction at first, and no crystals appear until evaporation has taken place, then around the circumference

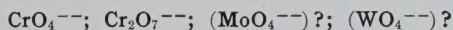
of the test drop disks appear. These disks are made up of fine needles. As the concentration of the drop rises through further evaporation, the disks grow fan-shaped and irregular.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a reaction strictly analogous to that obtained with $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, but the calcium salt is more soluble than that of barium and no crystals appear until the test drop has evaporated almost to dryness; then tiny disks, made up of exceedingly minute needles, form at the circumference of the test drop. These disks are much less refractive than those obtained with barium, and retain their circular form when the drop goes dry.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ produces a white "amorphous" precipitate, becoming granular and then distinctly crystalline in a zone around the granular deposit. Under a magnification of about $200\times$ the crystals are seen to consist of tiny dendritic aggregates or dendritic skeletons of very variable form.

5-With $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$ no precipitate is produced even in very concentrated solutions. As the test drop passes to dryness merely a crystalline crust is obtained at the circumference of the drop.

DETECTION OF THE ANIONS OF THE CHROMIUM GROUP



Chromates and bichromates are usually yellow or red salts, yielding yellow or red solutions. The bichromates are, as a rule, deeper in color than the chromates.

The alkali salts of both these ions are readily soluble in water; the salts of the alkaline earths are also soluble, but some of them are less soluble than those of the alkalis. Most other chromates and bichromates are difficultly soluble; a few are insoluble, but are readily soluble in HNO_3 . Insoluble chromates fused with KOH yield soluble K_2CrO_4 . Many bichromates are unstable and are decomposed by water. Basic, double, and polychromates are not infrequently met with.

Of the molybdates commonly encountered those of the alkali metals alone are easily soluble in water. Solutions of the alkali molybdates therefore give with solutions of the salts of other metals a precipitate of insoluble (or very difficultly soluble molybdates).

Di- and tri-molybdates are known and are more soluble than

the normal molybdates. Molybdates enter into the formation of many complex ions whose true natures have not yet been definitely established. Fortunately the analyst seldom has to deal with molybdates other than the alkali molybdates.

Dilute nitric acid added to a test drop containing a molybdate precipitates MoO_3 , soluble in slight excess of the acid.

Closely related to the molybdates are the tungstates, of which the orthotungstates derived from the acid H_2WO_4 and the metatungstates derived from the acid $\text{H}_2\text{W}_4\text{O}_{13}$ are the best known. The paratungstates $R_{10}\text{W}_{12}\text{O}_{41} \cdot x\text{H}_2\text{O}$ are rare, and for the most part insoluble in water. Even the alkali paratungstates are only very slightly soluble in water.

The alkali orthotungstates are readily soluble in water, but most other orthotungstates are insoluble or nearly so. Most metatungstates are water-soluble.

The composition of tungstates varies greatly according to the conditions under which they are formed.

Soluble orthotungstates can be differentiated from soluble orthomolybdates by means of dilute HNO_3 added to the test drop by Method I. As stated above, the MoO_3 at first formed is soluble in excess of the reagent, but the white hydrated WO_3 precipitated by HNO_3 is insoluble in excess.

HNO_3 added (by Method I) to a test drop containing meta- or paratungstates causes no precipitate.

The water-soluble tungstates are white (colorless).

Chromates — CrO_4^{--} .

(a) — Group Reactions.

1—With AgNO_3 there is first formed a heavy dark red, "amorphous" precipitate of Ag_2CrO_4 . On standing there are formed, in the zone beyond the precipitate, slender needles, small irregular platelets and tiny acute rhomb-shaped dark red plates. There are also irregular plates and scales in a great variety of forms. The solubility of Ag_2CrO_4 is so low that the crystals are not well developed. The value of recrystallizing, or precipitating Ag_2CrO_4 in the presence of Ag_2SO_4 , with the formation of an isomorphous mixture of these two salts, has already been referred to, and is especially important when testing for CrO_4^{--} . (See Silver, page 252; Chromium, page 216. Fig. 170, page 327; Fig. 163, page 323.)

2-Ba(C₂H₃O₂)₂ yields a fine granular precipitate, faintly yellow in color, and slowly becoming crystalline. The crystallization is most marked in the outer zone. Tiny irregular crystalline masses of variable outline are formed, together with tiny clumps of dendrites made up of rough needles. Some of these needles form radiates.

3-With Ca(C₂H₃O₂)₂ there is no precipitate, and no separation of crystals takes place on standing.

4-Pb(C₂H₃O₂)₂ produces, at once, a heavy bright yellow gelatinous precipitate that undergoes no change on standing.

5-Tl(C₂H₃O₂) yields a bright yellow gelatinous precipitate like that obtained with Pb(C₂H₃O₂)₂, but on standing the precipitate becomes granular and slow crystallization takes place with the formation of groups and tufts of fine needles and mossy radiates.

(b)-*Reaction with Manganese.*

Mn(C₂H₃O₂)₂ produces at once a dark brown "amorphous" precipitate, slowly becoming crystalline in part. In the outer zone tufts and clumps of very fine short needles appear, followed by radiates and bristling very dark brown opaque masses. The size of the needles and the character of their grouping varies with the concentration (Fig. 123, page 209).

With MnSO₄ no precipitate is at first formed, but on standing moderately large radiates of pleochroic needles separate. Sheaves and irregular tufts are also formed.

The reaction with manganese salts affords a ready method for differentiating between CrO₄⁻⁻ and Cr₂O₇⁻⁻, for with the latter no crystals are obtained.

The test should be performed in strictly neutral or slightly alkaline solutions.

Bichromates — Cr₂O₇⁻⁻.

(a)-*Group Reactions.*

1-AgNO₃ added by Method I to the "neutral" test drop gives an instantaneous dark-red precipitate, crystallizing almost immediately in slender dichroic prisms, thin plates, and rectangular tablets; many large but thin irregular scales are also formed.

2-Ba(C₂H₃O₂)₂ yields a granular precipitate in which no definite crystal forms can be observed. Although BaCrO₄ is formed it does not crystallize as well as when precipitated by CrO₄⁻⁻.

3- $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives no precipitate, and no crystals separate on standing.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives PbCrO_4 as a bright-yellow gelatinous mass, undergoing no change on standing.

5-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ a yellow and an orange precipitate is obtained, at first "amorphous," later becoming granular. Crystallization takes place less readily than in the case of CrO_4^{--} .

(b)- $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives no precipitate and there is no separation of crystals (distinction from CrO_4^{--}), but as the test drop passes to dryness a few tiny very dark brown (practically black) more or less spherical granules appear in little patches at the circumference of the drop and finally a ring of dark brown colloidal material is formed around the circumference of the test drop.

When MnSO_4 is employed instead of the acetate, no precipitate, no separation of crystals or granules and no brown ring is obtained.

(c)-The reaction of mercurous salts toward $\text{Cr}_2\text{O}_7^{--}$ ions in HNO_3 solution has been discussed under Mercury, page 149. It is, however, difficult so to adjust the condition as to obtain characteristic crystals of the mercury salt, and the test can be regarded in the light of a confirmatory test only (Fig. 90, page 137).

Molybdates — (MoO_4^{--})?

(a)-Group Reactions.

1-With AgNO_3 by Method I a yellow "amorphous" precipitate is produced.

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a white thick heavy "amorphous" precipitate with a tendency to become granular. No definite crystals can be discerned.

3-With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ a fine white granular precipitate is obtained, and on standing tiny colorless disks appear which require a magnification of 200 to 300 $\times$ for their resolution.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a heavy white gelatinous or curdy precipitate, undergoing no perceptible change on standing.

5-With $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ there is first obtained a white granular almost "amorphous" precipitate. In a few seconds crystallization in the outer zone takes place and small colorless hexagonal plates and tablets appear; at the same time large dendritic masses composed of irregular hexagons are formed upon the granular precipi-

tate. As the test drop passes to dryness it becomes filled with irregular scales and imperfect hexagons (Fig. 120, page 209).

(WO_4^{--})? gives a similar reaction, but thallos tungstate is slightly less soluble than thallos molybdate and hence the hexagons are not apt to be so well developed under like concentrations (Fig. 121, page 209). These two salts appear to be isomorphous.

(b)—*Reaction with Phosphates.*

To the test drop, add by Method I a solution of $\text{H}_2\text{NH}_4\text{PO}_4$ acidified with HNO_3 . Warm *gently*. A fine granular, bright-yellow precipitate developing into crystalline granules is obtained. (See PO_4^{--} , page 313. Fig. 124, page 223.) Under proper conditions (WO_4^{--})? may give an analogous reaction, but the precipitate is practically colorless.

When the reagent flows into the test drop, the HNO_3 usually first precipitates white hydrous MoO_3 or WO_3 . The MoO_3 dissolves in the excess of acid, and on warming the phospho-compound results; but because the heavy precipitate of MoO_3 prevents a free flow of the acid into the test drop the precipitate obtained is usually partly MoO_3 , white, and partly phosphomolybdate, yellow. Since hydrous WO_3 is practically insoluble in HNO_3 , the formation of a phosphotungstate is highly problematical, and when the preparation is heated the "amorphous" WO_3 turns yellow. The change from the white compound to the yellow requires a temperature almost to the boiling point. It is therefore highly important that in this test the preparation shall never be more than *very gently warmed*. A further precaution is essential: a test drop must always be tested with dilute HNO_3 before the phosphate-nitric acid reagent is employed, in order to ascertain whether a precipitate is produced by the acid alone.

Since sodium phosphomolybdate is quite soluble, materials containing a large amount of sodium salts or consisting of Na_2MoO_4 rarely yield a decisive test unless repeatedly heated and the preparation is brought almost to dryness.

For the detection of molybdenum as a cation, see page 219.

Tungstates — (WO_4^{--})?; ($\text{W}_4\text{O}_{13}^{--}$, $\text{W}_{12}\text{O}_{40}^{--}$, $\text{W}_{12}\text{O}_{41}^{--}$).

(a)—*Group Reactions.*

1—With AgNO_3 orthotungstates yield a heavy cream-colored "amorphous" precipitate which undergoes no perceptible change

on standing. A similar precipitate is obtained with metatungstates, but in a short time squares and rhombs appear, growing into small, colorless, highly refractive octahedra; at first most of the octahedra are malformed, but they soon fill out, and as the test drop passes to dryness well-formed crystals separate in large numbers. Paratungstates give no crystals.

2-With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ orthotungstates give a granular precipitate changing in part to colorless drusy, very tiny, lenticular grains, grouping themselves into spreading irregular aggregates. Meta compounds yield "amorphous" precipitates becoming granular, and under favorable conditions a few tiny disks are formed. No recognizable reaction is obtained with paratungstates.

3-With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ no definite crystals are obtainable. On standing a few colorless tiny disks are obtained with orthotungstates, but nothing with meta- or paratungstates.

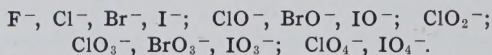
4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives gelatinous or somewhat granular precipitates with all tungstates, but no crystals separate.

5-With orthotungstates $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)$ gives hexagonal plates and tablets similar in appearance to those obtained with orthomolybdates, but in the case of (WO_4^{--}) ? there is a greater tendency to produce skeleton crystals (stars and rosettes). (Fig. 121, page 209.) No hexagons are obtained with meta- or paratungstates, and no definite crystals; an "amorphous" or granular precipitate only is obtainable.

(b)-Tested with a soluble phosphate in HNO_3 solution tungstates give a white "amorphous" or granular precipitate, which may develop into tiny colorless disks. A bright-yellow precipitate is never obtained, nor are crystals formed of definite shape.

Sodium salts prevent the precipitation of ammonium phosphotungstates, but do not interfere with the precipitation of hydrous WO_3 by HNO_3 .

DETECTION OF THE ANIONS OF THE HALOGEN GROUP⁷



Although the halogens present many striking relationships to the chemist, these same family resemblances are likely to be rather serious obstacles in the development of microscopic tests for their

⁷ Mason: *Mikrochemie* **4**, 145-148 (1926).

Chamot and Mason: *idem.* **5**, 85-101 (1927); **6**, 82-91 (1928).

identification. Most microscopic tests involve the formation of a crystal form or habit, typical and characteristic of the substance sought. In the case of the compounds of the halogens, their close relationship according to their positions in the Periodic System manifests itself in a high degree of isomorphism of their crystalline compounds, and for this reason, similar salts are likely to be very much alike, not only in their crystalline character but also in their physical and chemical properties.

As a preliminary step in an analysis the authors have found nothing superior to the grouping offered by the Bunsen-Treadwell classification based upon the formation and properties of the silver (or barium) salts of the halogens, as already outlined (page 288). According to this classification the silver salts of the anions fall into one of three groups.

1—Silver salts insoluble in water and insoluble in strong nitric acid.

2—Silver salts insoluble in water but soluble in HNO_3 .

3—Silver salts soluble in water.

In the discussion which follows, unless otherwise stated, it is understood that when a substance of unknown composition is found to fall in one of the groups 1, 2, or 3, identity tests are to be made on *separate* portions of the original material; the grouping serving merely as a time-saving device.

The corresponding compounds of the halogens may best be considered together at first, as a means of illustrating their similarities and emphasizing what differences exist.

Halides — F^- , Cl^- , Br^- , I^- . — With the exception of fluorides, the gradation in the chemical and physical properties of the various halides is so perfect that the differences between them are more likely to be those of degree, rather than of kind. The isomorphism of their crystals is particularly striking, and as a consequence, little help is to be expected from tests depending on differences of crystal habit of different halides of the same metal. Silver chloride, bromide, and iodide are isomorphous, and are similar in crystallization. Their solubilities do not differ widely enough so that any dependable separation may be obtained by taking advantage of this property. In the case of some other metals, however, the solubilities of their halides differ more greatly, and distinctions may be based on this.

(a)-Group Reactions.

1- AgNO_3 gives no precipitate with fluorides. With Cl^- very fine-grained crystals, which develop into visible octahedra on standing, are obtained from solutions containing $> 0.5 \mu\text{g. Cl}$ per drop. (See Fig. 171, page 327.) Br^- yields much finer crystals, the form of which is rarely recognizable from solutions of concentration similar to the above. I^- gives a precipitate too fine for its form to be recognized, with a limit of about $0.02 \mu\text{g. of I}^-$ per drop. AgCl and AgBr may be recrystallized from NH_4OH solution, yielding more distinct octahedra, but their solubilities are not different enough to permit a separation by means of this solvent, nor even an indication as to whether the precipitate consists mainly of AgCl or AgBr . AgI is not sufficiently soluble in NH_4OH solution for recrystallization to take place, and the other silver halides may be extracted from it practically completely.

2- TlNO_3 gives with Cl^- , in concentrations $> 15 \mu\text{g. per drop}$, highly refractive isotropic octahedra, cubes, stars, and crosses, which are soluble in hot water and recrystallize from it as coarse cubes. (See Fig. 101, page 169.) Br^- behaves similarly, in concentrations $> 2 \mu\text{g. per drop}$; the crystals of TlCl and TlBr are so similar that the variations of habit ordinarily observed may be due as much to differences in concentration as to the presence of different anions. TlI is very much less soluble than the chloride or bromide, and precipitates as very minute cubes from solutions containing $> 0.4 \mu\text{g. I}^-$ per drop. This fine-grained precipitate may sometimes enable iodides to be distinguished from chlorides and bromides.

3- $\text{Pb}(\text{NO}_3)_2$ or $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives crystals with either Cl^- or Br^- ($> 100 \mu\text{g. per drop}$), which are highly refractive flat orthorhombic prisms, frequently having forked or pointed ends or showing skeletal markings on their faces (see Figs. 104, 105, page 169). Their solubility is appreciable, and they are readily recrystallized from hot water. With I^- distinctive crystals are obtained, in the form of thin yellow hexagonal plates (see Fig. 106, page 181). From very dilute solutions only a very fine-grained precipitate may be formed, but its color and iridescent or scintillating appearance by reflected light is characteristic. PbI_2 is a useful test for iodides in mixtures with the other halides, though of limited sensitivity ($10\text{--}20 \mu\text{g. I}^-$ per drop).

4-Mercuric salts give a fine-grained red precipitate of HgI_2 ,

the limit being about that of the PbI_2 test. (See page 146.) Cl^- and Br^- give precipitates only from concentrated solutions.

5- CuSO_4 gives a fine-grained yellowish precipitate of CuI , having about the above limit of sensitivity. (See page 147.) Cl^- and Br^- give no precipitates.

6- PdCl_2 yields a dark brown or black, very fine-grained precipitate with concentrations of $\text{I}^- > 0.7 \mu\text{g. per drop}$. (See page 264.)

(b)-Oxidation to the Free Halogen.

Differential oxidation of I^- to I_2 , or Br^- to Br_2 , without affecting the other halides present, is not possible without more precise control than is practicable on a micro scale. However, I^- and Br^- can be oxidized together in mixtures and the evolved I_2 or Br_2 identified. For this purpose KNO_2 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in acid solution, are suitable if the liberated I_2 is to be tested by starch in the same drop. If the oxidation is carried out in a micro-crucible (page 15) as is necessary when Br^- is present alone or in mixture with I^- or Cl^- , other oxidizing agents, such as $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_3 , or KMnO_4 in acid solution, or even less powerful oxidants, may be employed.

By removal of I^- and Br^- from mixtures of halides, Cl^- may be tested for with greater certainty than if these anions were present. Oxidation by boiling cautiously two or three minutes with 10 per cent (by volume) HNO_3 in a micro-crucible, until negative tests for Br_2 and I_2 are obtained, will leave Cl^- unchanged. The acid solution remaining may be tested for Cl^- with AgNO_3 . About one per cent of Cl^- in mixture with the other halides may be recognized by this procedure.

(c)-Specific Tests for Individual Halides.

Fluorine is distinctly different from the other halogens as regards its compounds and reactions, so that its analytical detection cannot be based on group reactions such as those discussed above. Fluorides may be recognized by their exceptionally low refractive indices and by the possibility of HF being liberated by a strong acid such as H_2SO_4 . The etching action of HF on glass may be used for identification, but more positive evidence is offered by the formation of fluosilicates of characteristic crystalline character. (See Fig. 35, page 61.)

Chlorides are indicated, but not identified, by their crystalline precipitates with Ag^+ , Tl^+ , or Pb^{++} . Bromides, and preferably

also iodides, must first be eliminated (by boiling with 10 per cent HNO_3) if these precipitates are to be ascribed to Cl^- . Since some Cl^- is almost always likely to be present with the other halides, a distinct test is more important than a faint one which might be due to traces of unremoved Br^- or I^- .

(1)—*Chromyl Chloride Reaction.*

The well-known chromyl chloride reaction may be carried out on a micro scale, and will serve to reveal the presence of any combined chlorine in the sample; it does not serve to differentiate between Cl^- , ClO_3^- , and ClO_4^- , however.

The unknown material, in solid form, is added to a hot mixture of chromic anhydride CrO_3 (or $\text{K}_2\text{Cr}_2\text{O}_7$) and concentrated H_2SO_4 in a micro-crucible. If a compound of chlorine is present CrO_2Cl_2 will be formed, and this will be volatilized (b.p. 115°) and may be "fixed" in a small drop of NH_4OH on the under surface of the cover-slide. Since the CrO_2Cl_2 vapor is heavy, it is well to allow a minute or two for it to diffuse into the test drop, or *cautious* heating may be employed; tilting or rocking the crucible will aid the diffusion. The least spattering renders the test useless, for the H_2CrO_4 in the test drop will give the same reactions as would CrO_2Cl_2 . SO_3 is also evolved, as are Br_2 and I_2 if Br^- and I^- were present. The presence of CrO_4^{--} in the test drop, *provided no spattering has occurred*, indicates that CrO_2Cl_2 has been formed, which must have come from a chlorine compound.

If an excess of solid AgNO_3 is added to the neutral or acid test drop, containing CrO_2Cl_2 (or rather H_2CrO_4 and HCl , from interaction with water), AgCl (white) is first precipitated and when the precipitation of the chloride is complete the more soluble Ag_2CrO_4 separates as an orange to red precipitate, the color of which is readily observed against the white AgCl . Any Ag_2SO_4 formed by the action of the SO_3 will be colorless; any Br_2 or I_2 from the Br^- or I^- will be precipitated as AgBr or AgI . The only highly colored precipitate is the Ag_2CrO_4 . The identification of the Ag_2CrO_4 may be confirmed by recrystallization from NH_4OH . If the test drop is made strongly ammoniacal, all the precipitate (except AgI) will dissolve, and on exposure to the air the silver salts will be reprecipitated in more definite crystalline form. Silver halides will be formed first, in various modifications of the octahedron; Ag_2SO_4 and Ag_2CrO_4 , being isomorphous, will occur as mixed crystals, colored according to the proportion of Ag_2CrO_4

present. These may range from orange to deep red, and according to the intensity of the color exhibit pleochroism (red to orange). These crystals of $\text{Ag}_2(\text{Cr,S})\text{O}_4$ may occur as short orthorhombic prisms with pointed ends, as rhombs, or as dendritic and leaf-shaped forms, appearing first at the edges of the drop.

During the exposure of the NH_4OH test drop to the vapors from the crucible, the under surface of the slide should be watched carefully, so that if spattering occurs it may be observed and the drop discarded. It is well to examine the slide under the microscope also, to see if any yellow droplets of the chromic acid mixture have spattered up on its surface. If these precautions are taken, the CrO_2Cl_2 test is reasonably dependable, and its execution on a micro scale is only a matter of a few minutes.

In the presence of much Br^- or I^- , the test is best modified by oxidizing the bulk of the Br^- or I^- with H_2CrO_4 and *dilute* H_2SO_4 (1 : 4) first; little if any Cl^- is lost under these conditions. The heating during this oxidation serves to concentrate the H_2SO_4 , and an excess of CrO_3 and of concentrated H_2SO_4 is added to furnish the proper conditions for the formation of CrO_2Cl_2 , which is then driven off by gentle heating, and tested for as above. For critical work it is well to run a blank, to test out the H_2SO_4 , etc., employed, and in any case, one should consider only a distinct orange to red color of the crystals in the test drop as a positive test. The sensitivity of the CrO_2Cl_2 test is such that about 3 μg . of chlorine may be detected, but the presence of excessive amounts of Br^- or I^- decreases the sensitivity.

Bromides are not to be distinguished from chlorides by the group reactions mentioned above. The identification of free Br_2 is the most conclusive means of proving the presence of Br^- .

(1)—*With Starch.*

Br_2 may be indicated in high concentrations, (> 100 μg . per drop) by a yellow color with the starch used in testing for I_2 , provided the latter is absent. (See page 346.)

(2)—*With m-Phenylenediamine.*

A much more sensitive and reliable test depends on the formation of a characteristic crystalline precipitate of 2,4,6-tribromophenylenediamine, when Br_2 is brought in contact with a solution of *m*-phenylenediamine hydrochloride.⁸

⁸ Mason: *Mikrochemie* 4, 145-148 (1926).

The oxidation of Br^- to Br_2 is carried out in a micro-crucible, by means of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, or CrO_3 , in acid solution, or dilute HNO_3 . (See page 343.) Cl^- and I^- , if present, are likewise oxidized to Cl_2 and I_2 . The *m*-phenylenediamine hydrochloride, in a solution about $\frac{1}{20}$ saturated and to which a trace of H_2SO_4 has been added, is exposed to the liberated halogens as a tiny drop on the under surface of the slide which covers the crucible. Br_2 yields fine-grained crystals, if present in large amount, especially if the concentration of the reagent drop is high. When formed more slowly, or in an acidified solution of the reagent, the crystals are small fusiform needles, single and in clusters, highly refractive and strongly birefringent with parallel extinction (Fig. 172, page 327). Their formation may be observed through the slide without uncovering the crucible. Gentle warming is advantageous when small amounts of Br_2 are evolved, but it must not be carried to the point of causing steam to condense on the slide.

Cl_2 and I_2 give no such precipitate, though if present in large amount they may cause the formation of oily droplets which disappear on exposure to the air. An excess of I_2 may be removed by gradual addition of the oxidizing agent, with little loss of Br_2 ; the latter may be tested for during the evolution of the I_2 and will appear only when the oxidation of I^- is nearly complete. The limit of sensitivity is about $0.5\text{ }\mu\text{g}$. Br^- , except in the presence of a large excess of I^- . In mixtures with I^- , as little as one part in 500 may be detected.

Aniline hydrochloride may be used as a substitute for *m*-phenylenediamine hydrochloride; it gives a somewhat similar precipitate with Br_2 and none with the other halogens.

Iodides may be identified by means of the well-known coloration which free I_2 gives with starch.

(1)—*Oxidation to Iodine.*

The oxidation of I^- to I_2 may be carried out in a drop of solution on an object slide. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is a satisfactory oxidizing agent; KNO_2 is also suitable. To the solution to be tested, acidified with H_2SO_4 , add a few granules of starch⁹ and a fragment or

⁹ *Canna edulis*, arrowroot (maranta) or potato starches are more sensitive than others. Previous incipient gelatinization, by heat or by alkali, increases the delicacy of the test.

two of the oxidizing agent. Very gentle heating will hasten the reaction. If I^- was present the grains of starch will become blue to violet, and may be almost black if a large amount of I_2 is set free. In such cases free iodine is sometimes visible as a yellow zone in the solution, or even as minute acute rhombic brown crystals. A large excess of an alkali iodide may cause the starch to be colored reddish or brownish hues. The sensitivity of this test for I^- is about 0.8 $\mu\text{g.}$ of iodine, which is beyond the concentration at which Ag^+ gives a precipitate with I^- . The presence of other halides has little effect; one part of iodide in several thousand parts of bromides or chlorides can be detected.

(2)—Distillation in a micro-crucible affords a means of separating the liberated I_2 from any substances in the unknown solution which might interfere with the "starch-iodide" test. The oxidation of I^- to I_2 is carried out as in the case of Br^- . The above oxidizing agents may be used, or others such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_3 , PbO_2 , preferably in acid solution. Cautious heating aids in volatilizing the I_2 , which comes in contact with a tiny drop of water containing a few granules of starch, on the under surface of the slide covering the micro-crucible. The coloration of the starch may be followed without uncovering the crucible.

This modification of the test permits the identification of about 1.5 $\mu\text{g.}$ of I . The other halides decrease the sensitivity very little, unless present in large excess. It is desirable that the oxidizing agent should not liberate too much Br_2 or Cl_2 , or oxidation to IO_3^- may take place; for this reason $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KNO_3 , or $\text{K}_2\text{Cr}_2\text{O}_7$ are preferable to stronger oxidizing agents such as KMnO_4 .

(3)—The specific oxidation tests for Br^- and I^- may be utilized to test for other halides. For example, if KBr and *m*-phenylenediamine are both present in the test drop and a strong oxidizing agent is used, Cl^- may be identified, if Br^- is known to be absent. Similarly KI and starch may be used to identify Br^- or Cl^- , if only one of these is present. It is also possible to test for Br_2 and I_2 simultaneously with a single oxidation, by placing a drop of *m*-phenylenediamine hydrochloride solution and one containing starch grains side by side on the slide which covers the crucible.

Hypohalites — ClO^- , BrO^- , IO^- . — Strictly speaking, these salts belong with those of the acids whose silver salts are soluble in water, but this classification is of little use in analysis, for the

instability of the hypohalites is such that they are in effect characterized more by their oxidizing power and by their decomposition products, than by the reactions of the theoretically pure compounds themselves. Hypohalites are present in any solution of a halogen in water, and conversely their solutions decompose readily on acidification to liberate the halogen. Heating a solution of a hypohalite causes it to be transformed to a mixture of the corresponding halide and halate; thus a hypochlorite will give a precipitate of AgCl with Ag^+ , and a hypoiodite, one of AgI and AgIO_3 . The identification of the decomposition products of the hypohalites is simple. But since these decomposition products alone do not identify the hypohalite, evidence of its oxidizing power is necessary.

Solutions of hypohalites ordinarily smell of the free halogen; even such a weak acid as H_2CO_3 decomposes hypochlorites, forming HClO , which is unstable and gives off Cl_2 . Any tests employed for the identification of the free halogens are best carried out in test drops, exposed to the hypohalite contained in a micro-crucible.

Cl_2 from decomposition of hypochlorites may be identified by the precipitate of AgCl which it gives with a test drop of AgNO_3 , or by similar reactions with Pb^{++} or TI^+ . The fact that the chloride is the only substance precipitated (any chlorates formed being soluble) is distinctive, since Br_2 or I_2 will give precipitates of bromates or iodates, in addition to the insoluble halide, and these may be recognized by their anisotropic character.

If Br_2 is known to be absent, Cl_2 may be recognized by its oxidizing action on KBr ; a test drop containing a little KBr and some *m*-phenylenediamine hydrochloride is exposed to the gas, and if Cl_2 is present a test for Br_2 will be obtained in the drop.

Br_2 from hypobromites is identified by the *m*-phenylenediamine reaction. The fact that insoluble AgBrO_3 is formed, as well as AgBr , is also of value.

I_2 from hypoiodites is recognized by the starch reaction; with AgNO_3 , AgIO_3 and AgI are precipitated. The other reactions for I^- may be applied, if desired, for confirmatory tests.

Chlorites are of rare occurrence, and are notably unstable, particularly in solution, so that they are not as likely to be present in an unknown as are the other halogen acids. Their decomposition to Cl^- and ClO_3^- is common, while their formation, generally

from chlorine dioxide, is very likely to be accompanied by the formation of ClO_3^- .

All chlorites are soluble except those of lead and silver. Of these two, $\text{Pb}(\text{ClO}_2)_2$ is the more useful in analysis, for it may be precipitated in very weakly acid solution and is moderately stable; but if the solution is more than slightly acid this salt is readily soluble, with the evolution of the gas ClO_2 and the formation of Cl^- in solution. $\text{Pb}(\text{ClO}_2)_2$ forms very fine-grained platelets and tiny prisms and crosses which are highly refractive and strongly birefringent.

AgClO_2 is formed only in alkaline solution and is moderately soluble; its habit appears to vary considerably with the conditions of precipitation, and it is probable that the composition of the precipitate varies also; but since only anisotropic crystals are obtained, this serves definitely to distinguish AgClO_2 from AgCl .

Halates — ClO_3^- , BrO_3^- , IO_3^- . — The analytical properties of the halates differ in that all chlorates are soluble while bromates and iodates form numerous insoluble salts. For this reason chlorates will be discussed separately.

Chlorates, because they form no insoluble salts, cannot be identified directly by precipitation tests, though this negative character is not without value. Recourse must be had to some indirect procedure, either oxidation or reduction of ClO_3^- , and identification of the reaction products.

(1)—*As Perchlorates.*

Chlorates may be transformed to perchlorates by heating to dryness with H_2SO_4 , but the HClO_4 formed is volatile, and may be lost. The H_2SO_4 is supposed to serve as a preventive of overheating, as well as to facilitate the reaction, but neither function is performed perfectly enough to make the transformation even approximately quantitative. The ClO_4^- formed is recognized by the precipitate it gives with K, preferably in the presence of MnO_4^- . (See Fig. 40, page 67.) In practice, the above method has many short-comings, and is not always reliable on a micro scale.

The oxidation of ClO_3^- to ClO_4^- by persulphates, using Ag^+ as a catalyst, does not appear to yield results suitable for micro-analysis.

(2)-Reduction to Chloride.

A more reliable method of identifying ClO_3^- is by reducing it to Cl^- . Hydroxylamine sulphate does not accomplish this, though it does reduce BrO_3^- and IO_3^- ; but sulphites, ferrous salts, or metallic zinc in acid solution are very effective. The Cl^- formed is identified in the usual way, with Ag^+ , Pb^{++} , etc. The zinc metal should be removed before the salts of the heavy metals are added, or these will be "plated out" and will not be available for the test. SO_2 is very useful for the reduction of ClO_3^- to Cl^- , when the introduction of a salt into the solution might be undesirable. It may be generated in a micro-crucible, and the drop to be tested exposed to the action of the gas, and then tested for Cl^- with Ag^+ , or the Ag^+ may be put into the test drop before it is exposed to the SO_2 . In either case sufficient HNO_3 must be present to prevent the precipitation of Ag_2SO_3 , which might be confused with AgCl formed from ClO_3^- .

The sensitivity of the reduction test for ClO_3^- is about 20 μg . per drop of solution.

Since AgBrO_3 is slightly soluble, especially in hot water, there is a possibility of BrO_3^- appearing in the group with ClO_4^- and ClO_3^- , though unless a very small amount of BrO_3^- is present it will have been identified in the group of acids giving silver salts insoluble in HNO_3 . If there is any question as to a positive test for ClO_3^- (by reduction) being due to BrO_3^- , the reduction test using *m*-phenylenediamine hydrochloride (see page 345), may be applied to the solution of AgBrO_3 , and thus even a small amount of BrO_3^- may be detected in the presence of ClO_3^- . If a small amount of ClO_3^- is present with a large amount of BrO_3^- the identification is less simple. The chromyl chloride test is applicable where no other compounds of chlorine are present. It is also possible to reduce BrO_3^- with hydroxylamine sulphate, which will not reduce ClO_3^- , precipitate and filter off the AgBr , and test for ClO_3^- in the filtrate by reduction with metallic zinc, or FeSO_4 , etc. This procedure is indirect, and is only moderately satisfactory on a micro scale.

(3)-Formation of ClO_2 .

The reaction of concentrated H_2SO_4 with a dry chlorate forms chlorine dioxide as well as HClO_4 , and the ClO_2 may be made the basis of a useful test. The deep yellow color of the ClO_2 , either as a gas, or better, dissolved in the H_2SO_4 , is apparent when the dry

residue of a drop containing about 30 μg . ClO_3^- is moistened with a small amount of concentrated H_2SO_4 .

ClO_2 , evolved in a micro-crucible, may also be recognized by means of a hanging drop test with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution. $\text{Pb}(\text{ClO}_2)_2$ is formed, as described under the reactions of chlorites.

A-Group Reactions of Bromates and Iodates.

1- AgNO_3 gives with bromates, colorless crosses and short pointed tetragonal prisms, appearing almost opaque on account of their high refractive index; they are moderately birefringent and show parallel extinction. AgBrO_3 is appreciably soluble in water, especially if warmed, and may be recrystallized by cooling. It may also be separated from AgIO_3 fairly well by extraction. The limit of precipitation is about 40 μg . BrO_3^- per drop.

With iodates, AgNO_3 forms a fine granular precipitate, but in the presence of a small amount of HNO_3 characteristic acicular crystals, single and in radiating and flocculent masses, are obtained. They are highly refractive, with strong birefringence and parallel extinction. The sensitivity of this reaction is about 2 μg . IO_3^- per drop.

2-Barium salts give an appreciably soluble precipitate with BrO_3^- in concentrations greater than about 200 μg . per drop. Highly refractive monoclinic prisms, which show rather weak birefringence and an extinction angle of about 15° are formed. With IO_3^- , similar but less soluble crystals are obtained, as prisms, crosses, rhombs, and rosettes which grow more perfect on standing (Fig. 52, page 97). The sensitivity is about 20 μg . IO_3^- per drop.

Both $\text{Ba}(\text{BrO}_3)_2$ and $\text{Ba}(\text{IO}_3)_2$ tend to supersaturate, and crystallization may need to be encouraged by scratching the slide. The precipitate thus obtained clings to the glass, and may easily be washed by decantation. A confirmatory test with AgNO_3 may then be carried out, either in the saturated solution of the barium halates, or after dissolving them in a small amount of dilute HNO_3 . This permits a separation of BrO_3^- and IO_3^- from the halides or from IO_4^- .

3-Lead salts give, with BrO_3^- , prisms very similar to those of $\text{Ba}(\text{BrO}_3)_2$. With IO_3^- , a fine granular precipitate is obtained, which on standing develops into curving and branching forms.

Fine needles, radiating and in sheaves, are formed from more dilute solutions.

4-TiNO₃ yields furlings and clusters of cubes, moderately birefringent, with BrO₃⁻; and similar but less soluble and more branching crystals with IO₃⁻.

5-NH₄IO₃ and Ca(IO₃)₂ are insoluble enough to be precipitated from fairly concentrated solutions of iodates, whereas the corresponding bromates are soluble.

B-Reduction of Bromates and Iodates.

Reduction of BrO₃⁻ to Br₂, or IO₃⁻ to I₂, is a valuable means of identification, for the liberated halogen can then be recognized just as when obtained by the oxidation of halides. (See page 343.) A great number of reducing agents are suitable, but the best are hydrazine sulphate, hydroxylamine sulphate, phenylhydrazine hydrochloride, or hydroquinone. Nascent hydrogen, from zinc (plus a trace of a copper salt, to form a "couple") is the most satisfactory of the inorganic reducing agents. In carrying out the reaction it should be borne in mind that an excess of the reagent may carry the reduction so far as to form the halides instead of the free halogen. The solution should be acidified with H₂SO₄; gentle warming is advantageous.

The reduction of halate to halogen may be carried out in either of two ways:

(1)-In the same drop with the reagent used to test for the free halogen.

(2)-In a micro-crucible, with the test reagent in a hanging drop.

In applying the former of these methods to bromates, the organic reducing agents interfere with the *m*-phenylenediamine test for Br₂, so metallic zinc should be used for the reduction. The sensitivity of this method is about 30 μg. BrO₃⁻ per drop.

If the Br₂ liberated by reduction is identified in a separate drop, the choice of reducing agent is not restricted, and the method is of more general application. The solution to be tested is placed in a micro-crucible, acidified with H₂SO₄, and a fragment of the reducing agent is added. Cautious warming aids in liberating the Br₂. The test drop of *m*-phenylenediamine hydrochloride is employed just as in testing for bromides. (See page 346.)

In the case of iodates the choice of a reducing agent is not restricted, and the test with starch is practically as sensitive by

either method — about 4 μg . IO_3^- per drop. IO_4^- likewise yields I_2 on reduction, so its absence must be established by independent tests.

BrO_3^- and IO_3^- may be tested for simultaneously, by using two hanging drops of the appropriate reagents.

Periodates — IO_4^- .

A—With Silver Nitrate.

The physical chemistry of the silver periodates is somewhat in question,¹⁰ and the acidity of the solution has a marked effect upon the nature of the precipitate obtained with Ag^+ . From neutral or very slightly acid solutions of IO_4^- a precipitate is obtained which is satisfactory as a test, even though opinion is divided as to whether it consists of Ag_3IO_5 or Ag_5IO_6 . It is yellow to orange at first, fine grained, highly refractive, and probably owes its light color to its fine state of subdivision and high index of refraction. On standing, preferably on heating, the fine particles grow and their crystal form becomes apparent, while the color of the precipitate darkens nearly to black. No phase transformation seems to be involved, for the fine grains first formed, as far as can be observed, have a habit similar to the crystals developing later. These last are hexagonal and triangular plates and stars, which may change into snowflake forms. They are dark brown by transmitted light, or if finely enough divided, yellow. Birefringence is fairly strong. The precipitate may be dissolved in HNO_3 and reprecipitated by NH_4OH , but only fine crystalline grains are obtained by this procedure.

If the precipitation takes place in a solution containing an appreciable amount of HNO_3 a different type of crystals appears. These have been given the formula $\text{Ag}_2\text{H}_3\text{IO}_6$ (or $\text{Ag}_4\text{I}_2\text{O}_9 \cdot 3 \text{H}_2\text{O}$). The crystals are pale straw-yellow, acute rhombohedral in habit, exhibiting symmetrical extinction and fairly strong birefringence. They are very soluble in HNO_3 , and if more than a very small amount of the latter is present they will not be formed.

From solutions strongly acid with HNO_3 , or from HNO_3 solutions of either $\text{Ag}_2\text{H}_3\text{IO}_6$ or Ag_5IO_6 , a third type of crystals may be obtained. These are highly soluble, and are unlikely to occur in

¹⁰ Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, p. 410 (1922).

a test. They are tetragonal bipyramidal in form, and are isomorphous with KIO_4 , so their formula must be AgIO_4 . They are yellow in color, more soluble than KIO_4 , are highly refractive, and show strong birefringence. On the addition of water these crystals decompose to a fine-grained mass, composed of tiny but typical crystals of $\text{Ag}_5\text{H}_3\text{IO}_6$.

Of all the above precipitates, only the first is insoluble enough for a qualitative test, and it is suitable only under the proper conditions, namely, when the solution to be tested is neutral or *only very slightly acid*. Under these conditions a precipitate of Ag_5IO_6 may be obtained with concentrations corresponding to about 20 μg . IO_4^- per drop. If more than a very small amount of acid is present, only very concentrated solutions of periodates are likely to give a precipitate. The color of the freshly precipitated, finely subdivided Ag_5IO_6 , and its subsequent development of characteristic crystals, with darkening color, are typical, and serve to identify IO_4^- . The only other colored silver precipitate likely to be confused with the Ag_5IO_6 is Ag_3AsO_4 , but since this is much less readily soluble in HNO_3 , forms crystals bristling with long slender needles, and may be identified by other tests, AsO_4^{---} is not likely to lead to error. Ag_2CrO_4 , and $\text{Ag}_2\text{Cr}_2\text{O}_7$ are also colored, but they do not exhibit any sequence of color changes, are of entirely different crystal habit, and unless so thick as to appear opaque, are of a clearer, much more reddish hue by transmitted light.

B-As confirmatory tests for IO_4^- a number of reactions are available. K^+ gives with IO_4^- a characteristic precipitate of KIO_4 , acute tetragonal bipyramids, of fairly strong birefringence, not readily soluble in HNO_3 . These are obtained in concentrations greater than about 40 μg . IO_4^- per drop. Rb^+ and Cs^+ give similar crystals, rather more soluble in water. This precipitation of KIO_4 is of the same order of sensitivity as that of KClO_4 as a test for ClO_4^- , and is very distinctive, for acids giving potassium salts of such low solubility are few indeed.

C-Reduction to Iodine.

Periodates are reducible to iodine in much the same manner as are the iodates. (See page 352.) The iodine is identified by the starch reaction. It is possible thus to detect iodates in concentrations corresponding to about 20 μg . IO_4^- per drop.

This reduction is also applicable to the Ag_5IO_6 precipitate,

which is dissolved in a very slight excess of HNO_3 or H_2SO_4 , and acted upon by the reducing agent (hydroxylamine sulphate, metallic zinc, etc.). A very fine white precipitate of AgI is formed. The reaction with starch does not take place, probably because of the precipitation of all the iodine in the form of very insoluble AgI .

D—The fact that Ba^{++} gives no precipitate with IO_4^- aids in differentiation from IO_3^- , or in separating $\text{Ba}(\text{IO}_3)_2$ by precipitation so that the filtrate may be tested for IO_4^- with Ag^+ .

Perchlorates — ClO_4^- .

A—With Potassium.

The most distinctive reaction of the salts of perchloric acid is the formation of a characteristic precipitate with K^+ . Orthorhombic prisms and rhomb-shaped forms are obtained in well-crystallized habit (Fig. 40, page 67). These are isomorphous with KMnO_4 , and are readily colored (solid solution) by the latter if a little is added to the test drop. The test is thus rendered more easily observable. Skeleton forms occur if the concentration of ClO_4^- is high. (See also Potassium, page 69.) The limit of sensitivity of the above test is about 0.001 gram HClO_4 per cc. (50 μg . per drop).

B—Strychnine sulphate gives a precipitate of simple rectangular, lath-shaped forms with ClO_4^- . These have very weak birefringence, parallel extinction, and tend to grow in parallel clusters especially if the reagent is added as a solid. These crystals cross each other at right angles, overlying the fragment of strychnine sulphate, and giving an appearance similar to a frayed bit of cloth. The concentration of the reagent is best kept low. The sensitivity of this test is about 10 μg . per drop.

Other microscopic reactions of perchlorates are on record, but they are of questionable specificity.

Mixtures of Halogen Acids. — The following outline may serve as a guide to the identification of the anions of the halogen acids, especially in mixtures with each other.

Familiarity with the microscopic appearance of the precipitates formed by Ag^+ and Ba^{++} with the various acids may enable the analyst to go at once to specific confirmatory tests and thus greatly shorten the time required for the analysis.

To a drop of the neutral or only very slightly acid solution to be tested add AgNO_3 solution in slight excess.

A—No precipitate is obtained.

There may be present. ClO_3^- , ClO_4^-

1—Reduce and test for Cl^- .

2—Evaporate solution to dryness, add a drop concentrated H_2SO_4 ; there is evolution of ClO_2^- and formation of ClO_4^- on heating. ClO_3^-

3—Concentrate solution. Add K^+ and a very little KMnO_4 . Characteristic crystals. ClO_4^-

B—A precipitate is obtained IO_4^- , Cl^- , BrO_3^- , IO_3^- , ClO^- , BrO^- , IO^- , ClO_2^-

Note color and crystalline character of precipitate. Filter and wash precipitate. Test filtrate as in A.

1—Extract precipitate with dilute HNO_3 (1 : 10).

(a)—The precipitate dissolves. IO_4^-
Identify by reduction.

(b)—The precipitate is insoluble in HNO_3 ; extract repeatedly with hot water.

Concentrate extracts and test for. BrO_3^-

Confirm by reduction of original material.

2—Extract the precipitate with NH_4OH (1 : 4).

(a)—The precipitate is soluble. Allow the solution to evaporate at room temperature. Examine for crystals. Cl^- , Br^- , IO_3^-

Confirm IO_3^- with reduction test; Br^- with oxidation test; Cl^- with Ag^+ after removal of Br^- and I^- by oxidation.

(b)—A residue remains. I^- , (Br^-)
Confirm I^- with oxidation.

C—In all cases in which a precipitate has been obtained with AgNO_3 , test for the presence of. ClO^- , BrO^- , IO^- , ClO_2^-

In the Bunsen-Treadwell classification of acids the customary grouping on the basis of the solubilities of barium salts, while not so directly applicable to the identification of the halogen acids, should nevertheless be utilized in conjunction with the system outlined above.

The solubilities of the barium salts of the halogen acids are as follows:

Readily soluble in water: BaCl_2 , BaBr_2 , BaI_2 , $\text{Ba}(\text{ClO}_3)_2$, $\text{Ba}(\text{ClO}_4)_2$, $\text{Ba}(\text{IO}_4)_2$.

Very slightly soluble in water: $\text{Ba}(\text{BrO}_3)_2$.

Very slightly soluble in water, but soluble in dilute HNO_3 : $\text{Ba}(\text{BrO}_3)_2$.

Not readily soluble in HNO_3 : $\text{Ba}(\text{IO}_3)_2$.

Manganates — MnO_4^{--} ; MnO_4^- . — Few manganates or permanganates are known. Pure K_2MnO_4 and Na_2MnO_4 are water-soluble and stable in solution for a short time only. All other manganates of the common cations are practically insoluble in water or are decomposed by it.

AgMnO_4 is one of the few permanganates of low solubility.

Because of the intense color of most manganates and permanganates and their great tinctorial power in solutions, their presence is not easily overlooked. But a pink color does not necessarily mean that MnO_4^- ions are present, nor does an intense green prove the presence of MnO_4^{--} . There must be proof of the presence of manganese. (See page 232.) In this connection the isomorphism of perchlorates and permanganates is especially valuable.

Permanganates — MnO_4^- . — Specific tests applicable to dilute solutions are not available. The pink color of the solution, discharged by reducing substances, and the identification of manganese are sufficient for the identification of this ion. For comparison with the behavior of the other ions the group reactions are indicated below.

A-Group Reactions.

1- AgNO_3 gives no precipitate in dilute solutions. In very concentrated test drops or as test drops pass to dryness, square and rectangular plates and tablets and irregular angular grains separate around the circumference of the drop. These crystals are so dark colored as to appear black by reflected as well as transmitted light.

2- $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ give no appreciable reaction. On standing a reduction of MnO_4^- by acetate ion takes place and a brown precipitate is formed.

3-Pb(C₂H₃O₂)₂ yields an instantaneous dark brown flocculent precipitate, changing in part into very tiny spherical granules.

4-Tl(C₂H₃O₂) yields black tiny irregular drusy grains and three-armed and four-armed crosses.

ORGANIC ACIDS

It is necessary to include among the inorganic acids a discussion of acetates, oxalates and tartrates because of the frequency with which salts of these acids are used as reagents in microscopic qualitative analysis.

All normal acetates are water-soluble. The least soluble are those of Ag⁺ and Hg⁺. The use, therefore, of acetates as reagents does not introduce an anion that may give rise to insoluble compounds nor introduce a strong acid.

Many double acetates are known.

The oxalates of the alkalis are water-soluble, but most other oxalates are insoluble. Many of these insoluble oxalates unite with soluble oxalates to form soluble double oxalates.

Both "normal" and "acid" oxalates are common; some of the latter are very complex.

No general statements are possible with reference to the solubilities of the tartrates, for the variations are so great that relative solubilities cannot be deduced from the position of the cations in the Periodic System.

Acetates — (C₂H₃O₂)⁻.

A-AgNO₃ added by Method I to a concentrated neutral test drops yields pearly scales of AgC₂H₃O₂ (Fig. 174, page 359). These soon develop into long thin plates with more or less irregular sides and ends. Many of these plates become six-sided with terminal angles of about 90°, and exhibit parallel extinction (Fig. 175, page 359).

B-To confirm the test add H₃PO₄ and distill off the HC₂H₃O₂, absorbing it in a hanging drop containing a trace of NH₄OH or NaOH. Test the hanging drop by one of the tests for acetic acid (acetates).

C-HgNO₃, added by Method I to a concentrated test drop, gives colorless plates and prisms. Six-sided prisms have their terminal

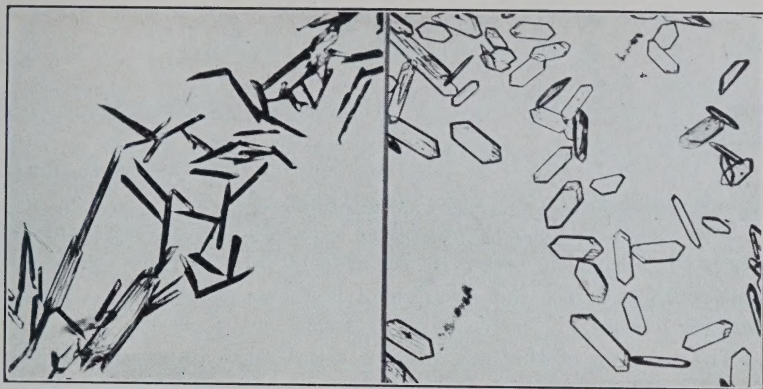


FIG. 174. $(\text{C}_2\text{H}_3\text{O}_2)^-$ with Silver Nitrate. 100 $\times$.

FIG. 175. $(\text{C}_2\text{H}_3\text{O}_2)^-$ with Silver Nitrate. 100 $\times$.

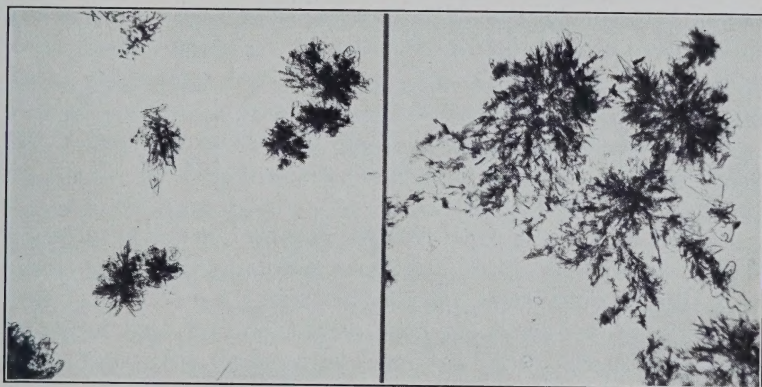


FIG. 176. $(\text{C}_4\text{H}_4\text{O}_6)^{--}$ with Silver Nitrate. 100 $\times$.

FIG. 177. $(\text{C}_4\text{H}_4\text{O}_5)^{--}$ with Silver Nitrate. 100 $\times$.



FIG. 178. $(\text{C}_4\text{H}_4\text{O}_6)^{--}$ with Lead Acetate. 100 $\times$.

FIG. 179. $(\text{C}_2\text{O}_4)^{--}$ with Silver Nitrate. 200 $\times$.

angles equal to 100° and exhibit parallel extinction (Fig. 173, page 327).

D—With NaCl and $\text{UO}_2(\text{NO}_3)_2$ sodium uranyl acetate is obtained. (See Sodium, page 52. Figs. 28, 30, page 53.)

The most satisfactory procedure is to add the uranyl nitrate (or better uranyl formate) to the drop of the unknown and draw this solution across the dry film of NaCl as described under the test for sodium.

The solution of the unknown material must be approximately neutral and must not contain free alkalis or mineral acids.

Oxalates — $(\text{C}_2\text{O}_4)^{--}$. — The appearance of the crystals obtained in testing for oxalates depends upon the nature of the cations present and the concentration of the oxalate ions. Acid, normal, and double oxalates, in stable and metastable forms abound, according to concentration and temperature conditions.

The statements given below apply to reactions obtainable with oxalates of the alkalis or ammonium. (See page 110.)

A-Group Reactions.

1—With AgNO_3 the usual reaction obtained is that of a heavy white “amorphous” precipitate soon becoming crystalline, especially in the outer zone. Crystalline grains are formed of very irregular outline, small dendritic masses abound, and here and there areas can be found consisting of irregular disks, and rhomboidal and hexagonal-shaped thin plates. The crystals are always very small and require a magnification of not less than $200\times$ to reveal their habit.

2— $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a granular precipitate, changing at once into long slender dendritic bunches of very fine needles. These develop into branching aggregates in wisps, crosses and radiates, the component arms of which may be straight or curved, rough, bristling, or branched. Their appearance is very characteristic and has already been referred to under barium, page 105. In a very short time the entire precipitate becomes converted into these peculiar dendritic aggregates (Fig. 62, page 103).

3—With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ a colorless sandy precipitate is first formed. In the outer zone there soon appear small bristling radiates, X's and skeleton crystals in thin irregular plates and scales; crosses are also formed. All crystals are very thin and never grow large (Fig. 60, page 103).

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a dense white curdy precipitate becoming sandy. A few small radiates and crosses can be found in certain restricted areas.

5-With $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)_3$ no precipitate is obtained and no separation of crystals until the test drop passes to dryness.

Tartrates — $(\text{C}_4\text{H}_4\text{O}_6)^{--}$. — The remarks made relative to the appearance of the crystals in testing for oxalates apply with equal force to the tartrates. The nature of the salt formed, whether an acid or normal tartrate or whether a double tartrate will be obtained, will depend upon concentrations and temperatures.

In order to obtain a separation of tartrates in a test drop, the solution must be practically saturated with respect to $(\text{C}_4\text{H}_4\text{O}_6)^{--}$.

A-Group Reactions.

1- AgNO_3 produces a flocculent white precipitate, instantly changing into large mossy radiates which appear to be light brown by transmitted light (Figs. 176, 177, page 359). There are also formed on standing stout very irregular angular prismatic grains. Short monoclinic prisms and "knee twins" of the bitartrate appear if the test is made in slightly acid solution. These prisms are strongly birefringent and are highly refractive.

2-With $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, no precipitate and no separation of crystals takes place, but on standing a very fine granular precipitate may form at the circumference of the test drop near where the reagent was caused to flow in. It is seldom that distinct crystals can be obtained. Usually when the drop goes to dryness nothing more than a crystalline crust is obtained.

3-With $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ the reaction obtained is usually similar in all respects to that given by $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, but if the very concentrated (with respect to $\text{C}_4\text{H}_4\text{O}_6^{--}$) test drop is run into a concentrated solution of a calcium salt there will be obtained after a short time large well-formed colorless highly refractive orthorhombic prisms. Since calcium tartrate is moderately soluble in water, but insoluble in alcohol, the addition of a little alcohol will cause the separation of crystals before the test drop passes to dryness (Fig. 70, page 113).

The presence of magnesium salts interferes with the separation of calcium tartrate.

4- $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ yields a heavy white curdy precipitate. On standing there are formed in the outer zone very characteristic

large, coarse, thick, dendrites composed of prismatic grains (Fig. 178, page 359).

5-With $\text{Ti}(\text{C}_2\text{H}_3\text{O}_2)$ no precipitate and no separation of crystals occurs unless there is a very high concentration of tartrate ions.

B-When a chloride of the potassium group is added to very concentrated solutions of tartrates, a separation of an alkali tartrate may occur, providing the conditions are favorable for the formation of an acid tartrate. (See page 72. Fig. 39, page 61.) If CsCl is employed it must be borne in mind that any one or more of very many double chlorides may be formed and separate in the test drop.

CHAPTER XII

SPECIAL REAGENTS YIELDING REACTIONS WITH A NUMBER OF CATIONS

There are a number of reagents and reactions of doubtful value as identification tests for specific cations or anions which are nevertheless of unquestioned usefulness in a preliminary study of mixtures of unknown composition since they may yield information which may materially shorten the time required for the completion of an analysis.

The most useful of these are hexamethylenetetramine, potassium ethyldithiocarbonate, fibers carrying zinc sulphide, and the precipitation of other metals by metals which are more electropositive.

In this same group can be placed benzidine hydrochloride and methylene blue, whose reaction products in microscopical qualitative analysis are of very doubtful value and uncertain composition but can be made to serve as indicators of the presence of oxidizing compounds.

Reactions Obtainable with Hexamethylenetetramine¹

Hexamethylenetetramine (methenamine, hexamethylenamine, formin, urotropin) has the formula $(\text{CH}_2)_6\text{N}_4$. It unites with many metallic salts to form direct addition products. When used in HCl solution as indicated below the compounds formed will have the general formulas $n[(\text{CH}_2)_6\text{N}_4 \cdot \text{HCl}] \cdot mR \cdot x\text{H}_2\text{O}$, where R stands for the chloride of the cation. In many cases more than one crystalline compound may be formed according to conditions; that is, the ratios of n to m will differ in the compounds which separate.

The reaction products indicated below are obtainable only

¹ Vivario and Wagenaar: *Pharm. Weekblad*, **54**, 157 (1917); *Chem. Zentral.* **88**, 224 (1917); *Zeit. anal. Chem.* **58**, 228 (1919); **67**, 298 (1925).

Denigès: *Schweiz. Apoth. Zeit.* **57**, 497 (1919).

Cole: *Philip. Journ. Sci.* **22**, 631 (1923).

Martini: *Addenda a la Microquímica Especial* (Cordoba, 1926); *Mikrochemie* **6**, 28 (1928).

when the following conditions are strictly adhered to. The test drop must be moderately dilute when the reagent is added. The test drop must be strongly acidified with HCl (1 : 3) and thoroughly mixed. A *large* fragment of the reagent is then introduced into the center of the drop and the preparation allowed to stand undisturbed for a few seconds and then thoroughly studied. The preparation is set aside and again carefully scrutinized from time to time until it passes to dryness. These repeated studies are essential because several different addition products may be formed as the concentration of the test drop changes, and it is important to note any variation in crystal habit which may take place.

As the reagent fragment disintegrates it may give rise to well-formed crystals in a zone just around the fragment; as these crystals move out into the test drop they may dissolve and disappear, but may again separate around the circumference of the drop. To avoid errors the analyst should perform a "blank" with the reagent in HCl, so as to become familiar with the crystal habit of hexamethylenetetramine hydrochloride, which separates readily from drops strongly acidified with HCl. If a metastable solution results, crush a little of the crystalline crust which forms around the circumference of the drop. Four- and six-sided tablets and plates of the hydrochloride are obtained. Those with four sides generally exhibit oblique extinction, those with six sides, parallel extinction. As the preparation passes to dryness, hexagons and six-pointed rosettes appear. The crystals are strongly birefringent and show colors of high orders.

It is always wise to apply the reagent to a series of test drops of different concentrations.

The addition of HCl to the test drop may cause a precipitate before the addition of the hexamethylenetetramine. If so, any one or more of the following may be indicated.

Ag^+ , Hg^+ , Pb^{++} , $\text{TI}^+(\text{Cu}^+, \text{Au}^+)$.

SiO_2 from alkaline silicates or silicious material.

TiO_2 , CbO_2 , TaO_2 .

MoO_3 , soluble in excess of HCl.

WO_3 , from ortho- and para-tungstates, but not from meta.

TeO_2 from tellurates and tellurites.

As_2O_3 from arsenites.

Sb and Bi as basic chlorides.

The addition of the hexamethylenetetramine may give rise to the following phenomena:

I. *Colorless crystals.*

a. *Isotropic octahedra.*

Sb^{+++} In addition to cubic crystals, small highly refractive tablets and hexagonal prisms with parallel extinction and colors of high orders. Isotropic hexagonal plates, irregular feathery dendrites, foliated aggregates. All forms may be obtained in the same drop as the concentration increases. Addition of KI increases the sensitivity of the test.

Bi^{+++} A fine granular precipitate is first formed, soon giving rise to large colorless octahedra. No birefringent crystals are to be found (distinction from Sb^{+++}) and no hexagonal plates.

Sn^{++++} A fine granular precipitate developing into colorless octahedra usually somewhat smaller than those of Bi^{+++} . Solutions strongly acid with HCl favor the formation of octahedra.

Hg^{++} See remarks under *b*.

Tl^{+++} See remarks under *b*.

In^{+++} The octahedra formed are always small, with high index of refraction. Al^{+++} and Ga^{+++} give no perceptible reactions.

b. *Anisotropic crystals in plates, prisms, or needles.*

Zn^{++} Wisps and tufts of feathery crystals, acicular prisms and imperfect radiates. Parallel extinction. Crystals rarely form about the reagent but appear around the circumference of the test drop, only.

Cd^{++} Thick hemispherical masses of acicular crystals so fine as to appear brown by transmitted light. Drusy botryoidal masses. Crystals formed at circumference of test drop, rarely at center.

Hg^{+} (In HNO_3 solution.) An immediate separation of colorless elliptical plates uniting in loose

radiates. There are also formed short stout prisms with acute ends, X's, crosses, and stars. As the concentration rises large dendritic masses of badly developed prisms appear. All crystals are strongly birefringent and exhibit brilliant polarization colors.

Hg⁺⁺

Instantaneous separation of dendritic wisps, changing into foliated masses of rhombiform plates. These plates are usually attached to the reagent fragments. Birefringence weak. In the outer zone colorless highly refractive isotropic octahedra appear.

Tl⁺⁺⁺

Radiates of lenticular plates. The solution must be very dilute since the reaction product has such a low solubility that the reagent becomes instantly covered with a mass of fine needles preventing its solution. As the test drop goes to dryness highly refractive isotropic octahedra are formed.

Pb⁺⁺

(Solutions of Pb(NO₃)₂.) When not acidified with HNO₃, a granular precipitate soon changing into angular grains of very irregular shape. These grains are highly refractive and strongly birefringent. If the test drop is acidified with HNO₃ a separation of crystals is obtained only on long standing.

WO₃⁻⁻

Alkali meta-tungstates yield an instantaneous precipitate of tiny four-sided plates with incurving sides. There is usually a marked rhythmic separation of concentric rings of tiny angular grains in the outermost zone; these grow into tiny dendrites and thin plates or slender needles. Ortho- and para-tungstates are decomposed by HCl and WO₃ is precipitated.

(MoO₄⁻⁻)?

Solutions in which the MoO₃ at first precipitated is redissolved in HCl give an "amorphous" precipitate becoming granular. In the inner zone are formed masses of very tiny needles or tiny dendritic irregular radiates.

$\text{Fe}(\text{CN})_6^{----}$ Short stout prisms, lath-shaped crystals and six-sided plates or tablets. Some show strong birefringence and colors of high orders. Extinction oblique.

II. *Yellow crystals are formed in a zone about the reagent.*

Au^{+++}
 $(\text{AuCl}_4)^-$ (Solutions of chloroauric acid.) Radiates of slender yellow needles. Later pleochroic orange-brown tablets. Still later these tablets become covered with a coating of tiny reddish-brown needles. At the circumference of the test drop yellow dendrites separate. All are strongly birefringent.

Pt^{++++}
 $(\text{PtCl}_4)^{--}$ Small yellow highly refractive octahedra are first formed. On standing curious, curving, somewhat feathery dendritic aggregates appear.

VO_3^- An "amorphous" yellow precipitate is first formed, soon changing into small irregular lichen-like aggregates which are jet black by transmitted light. In the inner zone, plates and foliated masses, lath-shaped crystals with oblique extinction, rhombs, hexagons.

CrO_4^{--} In very concentrated solutions the reagent fragments become covered with a yellow or orange precipitate, followed by outgrowths of long dendritic crystals or small short prisms singly, in clusters or in radiates. In very dilute solutions no reaction is apparent until the test drop passes to dryness, when crystals resembling fish scales may appear.

UO_2^{++} A yellow gelatinous precipitate is formed about the reagent. On standing the precipitate disappears. No crystals separate.

V^{++++}
 (VO_3^-) A greenish yellow "amorphous" precipitate is formed around the reagent. No crystals appear.

$\text{Fe}(\text{CN})_6^{----}$ Anisotropic yellow hexagonal and rhomboidal plates and tablets exhibiting colors of low orders. As the drop passes to dryness highly refractive yellow anisotropic octahedra are formed.

III. *Red or Brown Crystals.*

- Ir^{++++} Instantaneous production of a brownish-red granular precipitate crystallizing in small crosses and dagger-shaped and three-armed skeletons. Angular grains and tiny octahedra also appear as the concentration rises.
- Pd^{++++} Granular light brown (buff) colored precipitate, soon changing into radiating mossy aggregates which are practically colorless by transmitted light. At the circumference of the drop thin faintly brown rhombs and foliated masses. Birefringence weak. Os in compounds other than osmates resembles Pd if reaction takes place in concentrated solutions.
- Rh^{+++} Instantaneous separation of a light brown "amorphous" precipitate. On standing, tiny irregular angular grains. Closely resembles reaction given by Ir but color is brown not red.
- SeO_3^{--} Selenites are reduced. Red granular Se separates.

IV. *Colored crystals are formed at the circumference of the test drop; but none in a zone about the reagent.*

- Cr^{+++} As the drop passes to dryness, curious, almost colorless, crystalline composite plates, resembling fish scales.
- Fe^{+++} Highly refractive yellow tablets and masses of plates and tablets; irregular yellow rosettes. Crystal forms variable.
- Co^{++} Blue plates; irregular dendritic masses.
- Ni^{++} Lenticular plates, practically colorless.
- Cu^{++} Very compact radiates of short stout yellow prisms usually terminating in square ends.
- SeO_4^{--} Selenates are sometimes partly reduced to Se in small areas of the crystalline crust at the circumference of the drop. When this occurs there will be seen spots of a red granular or flocculent precipitate.

V. *Yellow colored zone changing to plum color around the reagent.*

Ru^{+++} A yellow zone is first formed around the reagent fragments; this color slowly changes to a dirty blue or plum color. Sometimes tiny dark colored stars and irregular angular grains are also seen. After the test drop has passed substantially to dryness the blue hue is most readily discerned. Hold over a white background.

VI. *No apparent reaction results from the introduction of the reagent.*

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ .

Ca^{++} , Sr^{++} , Ba^{++} .

Be^{++} , Mg^{++} , Al^{+++} , Ga^{+++} , Cr^{+++} .

HgCl_2 , HgBr_2 , $\text{Zr}(\text{NO}_3)_2$.

Alkali salts of $(\text{C}_2\text{H}_3\text{O}_2)^-$; $\text{C}_2\text{O}_4^{--}$; $\text{B}_4\text{O}_7^{--}$; SO_4^{--} , SO_3^{--} , Cl^- ; Br^- , I^- , F^- , $\text{Cr}_2\text{O}_7^{--}$.

OsO_4 and alkali osmates (see Pd).

**Reactions Obtainable with Potassium Ethyldithiocarbonate
(Potassium Xanthate) $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CS}\cdot\text{SK}$.²**

At the center of a moderately concentrated test drop of a "neutral" solution of the chlorides of the cations add a large mass of the fine felted needles of potassium xanthate. Observe the appearance of the preparation at once over a white and also over a black background. Then examine the preparation under the microscope. Allow the preparation to stand a few minutes and again examine it under the microscope.

By "neutral" solution is here meant the solution of the normal salt without any excess of free acid. Free acids, and even the "acidity" of certain salts, decompose the reagent with the formation of what appears to be a white precipitate but which under the microscope is seen to consist of tiny globules of a colorless oily liquid.

Since a considerable portion of the reagent is likely to be decomposed, it is essential that a much larger amount of the reagent

² Kotten: *Chemist-Analyst*. No. 48, Nov.-Dec. 1926, has suggested this reagent for macroscopic qualitative analysis.

must be used than is usual in microscopic reactions. When the oily droplets are so finely dispersed as not to be resolvable by a magnification of $200\times$, the reaction product appears to be an amorphous white precipitate and has been so recorded in the tabulation given below. With the chlorides of certain cations the emulsion persists, apparently, independent of such concentrations as are practicable in analysis, with others the dispersed droplets unite forming oily drops of considerable size, and these in turn may unite to form large patches floating about or more often moving to the circumference of the test drop.

I—White (colorless) precipitate, or colorless oily drops due to decomposition of reagent. No crystals formed.

Be^{++}	Oily drops, reagent decomposed.
Zn^{++}	Heavy "amorphous" precipitate.
Al^{+++}	Very fine "amorphous" precipitate, agglutinates on standing.
Hg^{+}	(Solution of HgNO_3 .) White "amorphous" precipitate, sometimes with yellow patches.
Tl^{+}	(Solution of TlNO_3 or $\text{Tl}_2(\text{SO}_4)$.) Dense gelatinous or curdy mass.

II—White (colorless) precipitate. Crystals formed.

Cd^{++}	Heavy white "amorphous" precipitate becoming granular. On standing disk-like radiates of short very fine needles, and in outer zone dendritic radiates, as evaporation takes place.
Pb^{++}	Oily drops in outer zone. Inner zone, bundles, wisps, and radiates of fine needles.
Sb^{+++}	(Solution containing free HCl .) Oily drops in outer zone; inner zone large colorless or slightly yellow prisms and plates.

III—Yellow precipitate, or yellow oily drops. No crystals.

Sn^{++}	Bright yellow oily drops; resembles Bi^{+++} reaction, but differs in that oily material does not crystallize.
Sn^{++++}	Behaves like Sn^{++} .

Cu^{++}	Bright yellow "amorphous" precipitate, changing slowly to orange.
Ag^+	Bright yellow "amorphous" precipitate, changing to brown and finally to black.
$(\text{PtCl}_6)^{--}$	Bright yellow "amorphous" precipitate. (Crystals of K_2PtCl_6 separate.)
OsO_4	Faint yellowish-white opalescence, usually invisible under microscope; visible against black background. On standing agglutinates into "amorphous" masses.
$\text{Fe}(\text{CN})_6^{---};$ $\text{Fe}(\text{CN})_6^{----}$	} Brownish-yellow "amorphous" precipitate. See IX.
$\text{Cr}_2\text{O}_7^{--}$	
	Light yellow "amorphous" precipitate, changing into brown.

IV—*Bright yellow precipitate or yellow oily drops. Crystals are formed.*

Bi^{+++}	Bright yellow oily drops in which crystallization takes place in a few minutes, with the formation of strongly birefringent, very fine needles in irregular radiates.
Tl^{+++}	If insufficient reagent is added the bright yellow "amorphous" precipitate first formed slowly fades to white, and colorless anisotropic hexagonal plates and masses or radiates of fine colorless needles appear. More reagent regenerates the yellow salt; yellow oily drops are formed, and bright yellow moderately birefringent irregular angular grains or masses of very fine dendritic needles or lichen-like radiates. All types may appear in a single preparation. In general the character of the yellow precipitate varies with the concentration of Tl^{+++} and of the reagent.

V—*Brown precipitate. No crystals.*

Fe^{++}	Brown "amorphous" precipitate, becoming black.
Ni^{++}	"Amorphous" brown precipitate.

Pd++++	Brown or buff "amorphous" precipitate in outer zone; on standing becomes granular. Inner zone "amorphous" precipitate mixed with yellow viscous oily drops; on standing these solidify and between crossed nicols are seen to be crystalline, but crystals do not grow to a size to be distinguishable by nonpolarized light.
Rh+++	Reddish brown "amorphous" precipitate.
Au+++	Reddish brown "amorphous" precipitate.
	Not same hue as given by Rh.
Cr+++	Faint brownish opalescence.

VI—*Brown precipitate. Crystals formed.*

Fe+++	Very dark brown (or even black) "amorphous" precipitate, and brown or black oily drops. On standing these drops unite forming yellow-brown or black (by transmitted light) oily patches in which thin lath-shaped yellow-brown pleochroic crystals appear.
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VII—*Black precipitate. No crystals.*

Fe++	(See under V.)
Hg+	(Solutions of HgNO_3 .) Black "amorphous" precipitate, and black oily drops.
Co++	Black "amorphous" precipitate.
V+++	Black glutinous "amorphous" precipitate and black oily drops. The precipitate is in reality dark green (?) but is so opaque and dark colored as to appear to be black. The oily drops solidify to a crystalline solid but its habit <i>cannot</i> be discerned under the ordinary conditions of testing.
V+++++	

VIII—*No precipitate is produced, but on standing crystals separate.*

Mn++	Large yellow monoclinic (?) prisms and tablets, strongly birefringent, or thin lath-shaped yellow crystals around the circumference of the test drop.
VO_3^-	Colorless or faintly yellow foliated prism-like aggregates, often growing to a considerable size.

IX—No visible reaction.

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ .

Ca^{++} , Sr^{++} , Ba^{++} , Mg^{++} .

Cl^- , Br^- , I^- .

$(\text{MoO}_4^{--})?$, CrO_4^{--} , $(\text{Fe}(\text{CN})_6)^{--}$. Sometimes brownish yellow precipitate if concentration high.

X—Deep blue precipitate.

Ru^{+++} Dark blue heavy granular precipitate.
As test drop goes to dryness color changes to brownish black.

Separations of Metals Based upon Differences in Electrical Potentials

The elements can be arranged in a series such as that shown at the right of this page. Those at the top of the series are strongly electropositive (less "noble"); those at the bottom strongly electronegative (more "noble"). The transition from plus to minus occurs, in the series as given, at cobalt.

The point at which the change of sign from plus to minus occurs depends upon the basis of classification used and the system employed for the calculation of the numerical values of the electropotentials of the different members of the series.³ In most tables which have been published the change in sign from plus to minus takes place at H, and Co, Ni, Sn, and Pb are considered as electropositive.

The elements above hydrogen in the series can liberate hydrogen from an acid, but those falling below H, *i.e.*, which are more electronegative than H, do not normally give this reaction.

Theoretically any element in the series should be able to precipitate or replace, in an acid solution, any other element lower in the series (less electropositive). As applied in practice there are certain limiting factors which modify the character of the reaction;⁴ chief among these are the nature

Cs^+
Rb
K
Na
Li
Ba
Sr
Ca
Mg
Al
Cr
Mn
Zn
Cd
Fe
Ti
Co
Ni
Sn
Pb
H
Sb
Bi
As
Cu
Hg
Ag
Pd
Pt
Au
Ir
Rh
Os
Si
C
B
N
Se
P
S
I
Br
Cl
F⁻

³ For these numerical expressions of the electropotentials of the different members of the series, the reader is referred to any one of the more comprehensive text books on physical chemistry.

⁴ Mellor: *Inorgan. and Theoret. Chem.*, I, p. 1014.

of the metal used, the character of the solution (concentration, acidity, anions present), the temperature, etc.

In making use of this principle in inorganic qualitative analysis, a small, clean, bright fragment of the "reagent" metal is dropped into the somewhat concentrated test drop which has been acidified with HCl. The metal fragment should be small — not over 2 or 3 mm. long by about $\frac{1}{2}$ mm. wide and thick. It should be handled with forceps so as to avoid a coating of grease from the fingers, and must be completely "wetted" by the solution.

To obtain the best results and the formation of characteristic "trees," the test drop must be just barely acid, the reaction



FIG. 180. Silver Precipitated by Metallic Zinc. 50 $\times$.



FIG. 181. Tin Precipitated by Metallic Zinc. 50 $\times$.

must be slow, and the preparation must rest upon the microscope stage undisturbed.

Since a metal is precipitated upon the reagent in metallic crystals, the precipitate is opaque and all that can be seen by transmitted light is a black silhouette. To note the color, hue, and luster, and the full beauty of the crystals the preparation should always be examined by reflected as well as by transmitted light.

The deposited metal may crystallize either in (1) long, loose dendrites more or less arborescent in character and usually with straight, loose branches at right or acute angles to the main stem (Fig. 181), or the aggregates will resemble a fern frond or a branch of coral; or (2) the crystals may take the form of delicate, more

or less curving, feathery or mossy aggregates (Fig. 180, page 374); or (3) the "tree" may resemble the second type but the coating upon the reagent-metal is denser, less feathery, and the dendrites will be much shorter and coarser; or (4) the precipitated element may not form a "tree" but will merely plate or coat the reagent or may merely stain it.

Most of the metals depositing in compact short mossy trees can also yield trees of the loose feathery or fern-like type. Hence both the compact and loosely branched type may sometimes be obtained from the same test drop.

Elements that merely stain the zinc often fail to yield any perceptible reaction. The stain is readily overlooked as it forms only slowly and may be too thin to be discernible. Usually no stain is obtained until the free acid has combined with the zinc and the active production of hydrogen has ceased and the test drop has passed almost to dryness.

The introduction of metallic zinc into a test drop may sometimes lead to hydrolysis and the precipitation of a non-crystalline basic salt or a hydrous oxide.

The following tabulation of the phenomena produced when a fragment of metallic zinc is introduced into a weakly acidified test drop is offered as a guide which may prove useful in the analysis of materials of unknown composition.

If a precipitate is formed when the test drop is acidified with HCl (see page 364), use a HNO_3 solution containing only a bare trace of free acid, or decant, filter or centrifuge from the precipitate and test the clear solution with zinc. The precipitate is washed and analyzed separately.

"Trees" or stains upon the zinc should not be regarded as identification tests, but merely as a guide toward the better planning of a more logical method of attack than might otherwise be adopted.

The electromotive series may also be utilized as a guide to separation of certain metals, in eliminating interferences in analytical testing, or in concentrating or collecting a metal for identification. For example, copper may be removed by placing a drop of the solution on a sheet of zinc or iron, and decanting repeatedly until the metal is no longer blackened by the deposit. The use of copper as a means of concentrating mercury is discussed on page 142.

In any of the above applications it should be remembered that as one metal ion is discharged, the more electronegative metal passes into solution.

I—The “ tree ” is large and loosely branched.

The branches are simple and are usually straight, meeting the main rib at right or acute angles, and are rarely curved. Trees silvery with pronounced metallic luster.

Ag, Pb, Sn, Tl, In
(Sb, Bi,)

II—The “ tree ” is short, compact, mossy, but there may appear after long standing loose textured, slender, many-branched dendrites.

The short, compact, mossy type is usually black; the slender many-branched dendrites usually have a metallic luster and the color of the element deposited.

Sb; Bi; Cu; Te; Au; Pd.

III—The zinc is stained brown or black. No “ tree ” is formed.

Mn; Ni (Co gives no stain); Rh; Pt; Ir; V; U; Te; Se(red).

IV—Silvery white globules are formed.

Hg. The globules are opaque, black by transmitted light, and are distinguishable from bubbles of H_2 in that they have no bright center.

V—The zinc remains unaffected but the solution becomes colored.

Blue — Mo; Ru.

Brown — Ni; Ti.

Red — Ti.

Reactions Obtainable with Textile Fibers Impregnated with Sulphides⁵

Guncotton or wool fibers impregnated with zinc sulphide afford a ready and sensitive means of grouping the heavy metals in the same manner as is accomplished when using H_2S and $(NH_4)_2S$ in ordinary qualitative analysis.

The concentrated test drop is acidulated with HCl and into it

⁵ Emich and Donau: *Ann.*, **351**, 432 (1907).

Chamot and Cole: *Jour. Ind. Eng. Chem.* **9**, 52 (1918).

a long "sulphide-fiber" is introduced and thoroughly immersed. Warm very gently and examine at once.

If the fiber does not become colored, allow the preparation to evaporate to dryness, spontaneously. Apply a drop of NH_4OH (1 : 3), examine under the microscope, and add one or more fresh "sulphide fibers."

In HCl solution the fiber turns

Lemon yellow	As, Cd.
Straw yellow	Sn.
Reddish yellow	Sb, Bi.
Brownish yellow	Ag, Sb, Bi, Cu, Hg, Pb, Pt, (Mn, Fe, Co, Ni).
Black	Ag, Bi, Cu, Hg, Pb, Pt.

In HCl solutions no change in color, but on adding NH_4OH the fiber turns

Brown or black	Ag, Pb, Hg, Au.
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The zinc sulphide fibers should always be tested with known solutions before employing them in the examination of materials of unknown compositions, since the fibers do not always retain their original sensitivity when kept for long periods.

Free HNO_3 must be absent. To avoid the possible oxidation of ZnS to ZnSO_4 it is a wise precaution always to evaporate to dryness with HCl .

The reactions of properly prepared zinc sulphide fibers are very sensitive in HCl solutions, but far less so and rather unsatisfactory in NH_4OH solutions.

Colors and hues vary with the relative concentrations of the cations present in the test drop and with that of the ZnS in the fiber.

The value of the method lies in the rapidity with which an indication is obtained of the presence or absence of metals yielding colored sulphides.

CHAPTER XIII

QUALITATIVE ANALYSIS OF MATERIAL OF UNKNOWN COMPOSITION

A qualitative analysis is usually undertaken for one of the following reasons:

1-To establish fully the chemical constitution of the material under examination.

2-To establish the presence or absence of certain elements or radicals.

3-To test for the presence and nature of impurities.

Microscopic qualitative analyses in themselves yield only chemical information, and if they are to have maximum usefulness must be combined with observations of physical properties, in order that the identity of the actual phases present, and not merely the ions existing in solution, may be established. Furthermore, microscopic analytical methods are particularly appropriate in connection with studies in which the problem of sampling is difficult, and where the individual constituents of the specimen would otherwise have to be treated together instead of being capable of preliminary separation.

Sampling for microscopical analyses is likely to present different problems than in macroscopic analytical work. If any non-uniformity of composition exists, the aim of microscopical studies should be to detect it, and to ascertain the nature and extent of the local variations, rather than to insure an "average" sample, in which such significant inhomogeneities are too often completely masked.

Ordinarily, therefore, the sampling of any heterogeneous specimen involves a separation of its different constituents, and subsequent testing of some or all of these according to the procedure outlined on subsequent pages. Frequently the minute amount of sample required is the chief justification for the microscopical methods; in any case, sampling or separation are greatly simplified by the fact that a small specimen is sufficient and that only a

small quantity of each of its components need be isolated for chemical analysis.

Separation of powdered mixtures into their various ingredients should be accomplished whenever possible, for a reaction may take place between components when brought into solution, although the mixture may not interact when dry. Even if only one constituent can be separated pure, it should be identified in order that the remaining ones may be ascertained in the dissolved mixture "by difference."

Mixtures in which the different solid constituents are recognizable can usually be separated sufficiently for chemical tests, by rather simple means. (See *Vol. I*, pages 140-149.) Hand sorting, under a magnifier or a Greenough binocular microscope, will be adequate for all but very finely divided material, finely pointed forceps, a glass rod drawn to a point, platinum wire sealed to a piece of glass tube, or capillary pipettes will be found useful for picking up small grains. The rod or wire may be moistened by breathing on them, or rendered slightly sticky by a trace of oil, balsam, vaseline, or glycerine. A miniature spatula, hammered from heavy platinum wire, is convenient for handling particles of all sizes or for scraping up loose material. Dental chisels, needles, or diamond or "Carborundum" splints may be necessary for isolating particles from aggregates of hard material, such as refractories, ceramic products, minerals, and alloys. Preliminary crushing in a "diamond" or mineralogist's mortar, is often the simplest means of preparing hard and brittle specimens for hand sorting under the microscope.

Dissecting needles, preferably with spear or knife points, will serve for cutting out bits from specimens of soft material, scraping away the outer portion to expose the interior, or removing layers of protective coatings or adhesives.

When circumstances limit the quantity of material handled to a single speck, or when the specimen must not be appreciably damaged by the removal of the sample, special technique is necessary. "Chemical micrurgy,"¹ by means of the micromanipulator (see *Vol. I*, page 144) permits exceedingly minute particles to be handled, or microscopic drops of reagent to be applied for testing *in situ*.

¹ Titus and Gray: *Ind. Eng. Chem. (Anal. Ed.)* **2**, 368-71 (1930).

"Streaks" of alloys or minerals,² obtained by rubbing on a ground glass or silica plate, furnish material in finely powdered form, with minimum injury to the object studied.

A hypodermic needle, cut off squarely and sharpened, may be used like a "cork borer" to remove tiny "cores," as samples of paintings and other antiquities.³

Sifting or winnowing, heavy liquid flotation, or sedimentation in water or other liquid may afford a means of separating powdered mixtures, without the labor of hand sorting.

If the ingredients of a heterogeneous mixture are not readily separable, nor easily soluble, the possibility of testing *in situ* should be borne in mind. The action of the reagent on the individual portions of the sample can be observed under the microscope, and even a single test may afford some clue to the interpretation of analyses made on the mixture as a whole.

Suspended matter in liquids may be collected by sedimentation or by means of the centrifuge. If filter paper fibers are not objectionable, filtration according to the methods given on page 11 may be satisfactory for dealing with small amounts of suspension.

The study of the individual substances obtained for analysis should include physical and chemical observations.

Physical examination should cover the form, size, and distribution of the material. It may well be carried out in connection with sampling operations. The apparent purity of the specimen, or the presence of effloresced, deliquesced, or otherwise altered portions, will often be of significance. It should be remembered that physical examinations rarely use up much of the sample, and that any information which they yield is *in addition* to the chemical evidence.

Physico-chemical behavior indicating hydrates, double salts, or the presence of polymorphic substances is often highly significant (see *Vol. I*, pages 357-363) and should be studied as fully as possible, especially in those cases where the nature of a solid phase, rather than the presence of ions in solution, is to be determined. Many double salts, stable under controlled con-

² The use of streaks as samples for microchemical testing is discussed by Gaubert: *Comptes rendus* **177**, 960 (1923).

See also Strebinger and Holzer: *Mikrochemie* **8**, 264 (1930).

³ Laurie: *Pigments and Mediums of the Old Masters* (1914) p. 19; *The Analyst* **55**, 162 (1930).

ditions or when dry, cannot be dissolved and recrystallized without decomposition.

A crystallographic examination should always be carried out. (See *Vol. I*, page 315). Its completeness will naturally vary, depending upon whether the material is, or can be prepared, in suitable condition to allow the detailed determination of crystal form and optical properties, and also upon the needs of the analyst. Comparison with known samples, crystallized under similar conditions, may speed the course of the analysis greatly, when the possibilities are limited in number. Where reasonably full descriptions and numerical determinations of refractive indices are possible, recourse to published tables of properties may be sufficient for identification,⁴ or may greatly limit the required chemical tests.

When the material in hand is distinctly crystalline and isotropic, the authors believe that its identification can be more rapidly accomplished by first testing for the anions.

The number of inorganic salts which are isotropic (cubic system) is relatively small in comparison with the large number which are anisotropic. Often a determination of refractive index and reference to a table⁵ will afford an immediate clue as to the probable compound under investigation.

Having identified the anions present, a plan for the search for the cations can readily be made by consulting the following table which includes most of the isotropic inorganic salts.⁶

⁴ Winchell: *Optic and Microscopic Characters of Artificial Minerals*. See also the other works cited in *Vol. I*, pages 324-325.

⁵ Such as that of Winchell: *op. cit.*, p. 162.

⁶ Salts of the "rare earths" are not included in the tabulation.

ISOTROPIC INORGANIC SALTS

<i>Anion found</i>	<i>The Material may contain one or more of the cations listed below</i>
Arsenate	Na^+ (as $\text{Na}_7\text{F}(\text{AsO}_4)_2 \cdot 19 \text{H}_2\text{O}$)
Borate	Na^+
Bromate	Na^+ ; NH_4^+ ; Mg^{++} ; Zn^{++} ; $\text{Cd}^{++}(\text{?})$
Bromide	Li^+ ; Na^+ ; K^+ ; Rb^+ ; Cs^+ ; NH_4^+ ; Tl^+ ; Cu^+ ; Ag^+ ; $(\text{Si}; \text{Ge}); \text{Fe}^{++}$
Carbonate	$\text{Na}^+ \text{Mg}^{++}$, [as $\text{Na}_3(\text{CO}_3)_2 \cdot \text{MgCl}$]
Chloride	Li^+ ; Na^+ ; K^+ ; Rb^+ ; Cs^+ ; NH_4^+ ; Tl^+ ; Cu^+ ; Ag^+ ; Zn^{++} ; Sr^{++} ; Sn^{++++} ; W^{++++} ; $(\text{Pd}; \text{Ir}; \text{Pt}; \text{in complex ions with alkalis})$
Chlorate	Na^+
Cyanide	Na^+ ; K^+ ; Zn^{++}
Fluoride	Li^+ ; Na^+ ; K^+ ; Rb^+ ; Cs^+ ; NH_4^+ ; Ca^{++} ; Sr^{++} ; Ba^{++} ; Pb^{++} ; Fluo-silicates, -zirconates, -titanates of alkalis. Basic aluminum fluoride
Iodate	Al^{+++}
Iodide	Li^+ ; Na^+ ; K^+ ; Rb^+ ; Cs^+ ; NH_4^+ ; $\text{Cu}^+(\text{?})$
Nitrate	Ca^{++} ; Sr^{++} ; Ba^{++} ; Pb^{++}
Nitrite	Double or Triple Nitrites of Na ; K ; Rb ; Cs ; Tl^+ ; NH_4 with Pb ; Co ; Ni ; Cu^{++} , Hg^+ , Sr , Ba
Oxide	Cu_2O , MgO , CaO , SrO , BaO , NiO , CoO , B_2O_3 , As_2O_3 . SiO_2 when fused
Phosphate	$\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$; Ag_3PO_4 ; $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19 \text{H}_2\text{O}$
Selenate	Selenate "alums"; only a few are known.
Sulphate	Na^+ ; K^+ ; Rb^+ ; Cs^+ ; Tl^+ ; Ag^+ ; NH_4^+ ; Al^{+++} , Cr^{+++} , Fe^{+++} , Mn^{+++} , In^{+++} , Ga^{+++} , Tl^{+++} , Rh^{+++} , Ti^{+++} , V^{+++} in "alums" Mg^{++}
Vanadate	Na^+ ; Alkali fluovanadates
Silicate	Li^+ ; Na^+ ; K^+ ; Al^{+++} ; Cu^{++} ; Ba^{++} ; Mg^{++} ; Zn^{++} ; Fe^{+++} ; Silica gel

Chemical Examination. — The application of microscopic qualitative analytical tests to the identification of unknown material is likely to be of limited value if these tests are merely employed empirically, or as a part of some fixed analytical scheme. The reagents serve for so many different tests, and the possible appearances with each are so numerous, that the analyst must keep in mind all the various reactions which may occur, and must be alert to interpret the unexpected phenomena as well as the normal response to tests. The correlation of all the chemical evidence yielded by the application of one or two reagents may advance the analysis far beyond the direct "positive or negative" results of the tests.

To this end it is desirable that full notes of the results of all tests with group or specific reagents should be kept, especially since even negative evidence, or abnormal and unexpected precipitates, may acquire a significance and afford valuable confirmation in the light of subsequent operations. Furthermore, the evidence thus assembled in concrete form is particularly useful as an aid in deciding what crucial tests should be applied to decide doubtful cases. The analyst should never perform a test without having in his mind a clearly formulated question which he expects it to answer.

It is not possible to generalize as to whether one should test first for cations or anions. Whichever reactions seem most likely to yield conclusive information should be tried first. Sometimes it is quickest to carry out both types of tests more or less together; frequently the recognition or elimination of certain cations will immediately indicate the presence or absence of certain anions, and *vice versa*. A great saving of time will result if each step in the analysis can be utilized as a guide to the choice of the next, and can be correlated with those which have preceded it.

It is always wise to reserve the major portion of the sample, and to carry out the analysis on a fraction of it. If the analyst has schooled himself in carrying out tests on minute drops of solutions this will entail no hardship, and will insure that ample material is available for confirmatory reactions, or in case unexpectedly extensive tests need to be carried out. Similar precaution is advisable when dealing with filtrates or precipitates which are to be used for subsequent tests.

The slides, crucibles, and watch-glasses which serve as the apparatus of the analysis may conveniently be marked by a "glass marking" or "Carballoy" pencil, in order to avoid confusing preparations which are set aside for future study.

As a preliminary to the actual analysis, the common chemical properties of the material should be noted, such as solubility in various solvents and reaction with them, behavior on heating the dry substance and its solution, ease of sublimation or fusibility, acid or alkaline character of the aqueous solution, etc. Tables of properties⁷ will be found invaluable for reference in connection

⁷ Such as Segerblom: *Tables of Properties of Inorganic Substances*, and the larger works on inorganic chemistry and qualitative analysis.

with such examinations, and especially for confirming or disproving tentative identifications based on analytical reactions.

Reagents for microscopic analysis are ordinarily applied to material in solution, but fusion reactions and blowpipe tests may often be employed to great advantage, especially in dealing with minerals or relatively insoluble substances.

Where a **positive test** is obtained, the interpretation is usually simple, provided the analyst actually is familiar, from experience on knowns, with the character of the product. However, when a search is made for any particular element or radical, care should be taken that none has been introduced in the solvents, reagents, or apparatus used, or a positive test will be of doubtful meaning. For this reason blank tests run in parallel are always advisable in critical work.

Rough estimations of the amount of the substance present are often possible from the heaviness of the precipitate which it yields, and also from the limits of sensitivity of the various tests for the ion in question.

Where a definite **precipitate not recognizable** as due to any of the substances sought, occurs, several explanations are possible:

1-The reagent may be yielding a precipitate with the ion of opposite sign. For example, potassium mercuric thiocyanate as a test for cations in a solution containing an iodide would give a precipitate of mercuric iodide, which might be misinterpreted as indicating the presence of an ion forming an insoluble double thiocyanate.

2-Too concentrated solutions, resulting in too rapid precipitation, may have prevented the growth of crystals of a size adequate for recognition. The method of adding the reagent is an important factor in regulating the concentration gradient in the preparation. All parts of the test drop should be examined, since in some at least there are likely to be crystals of characteristic form.

3-The presence of a strong acid or alkali may prevent precipitation. This is particularly likely to occur if acid has been used to dissolve the material. For example, an insoluble phosphate, dissolved in HNO_3 , will yield no precipitate with AgNO_3 unless the free acid is neutralized. Buffer salts, such as $\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$, are often useful in lowering the hydrogen ion concentration of the solution sufficiently to allow precipitation to occur.

4—Other substances in test drops may interfere with the normal habit or color of the reaction product. Combinations of ions sometimes act in a manner not to be predicted from their individual behavior.

5—The precipitate upon which the test depends may be masked by the simultaneous precipitation of other materials. For instance, hydrous oxides may be precipitated in making the solution alkaline preparatory to a test.

6—Ions not ordinarily precipitable by the reagent may be present in excessive amount, and hence form relatively insoluble compounds or double salts of low solubility; or some substance may be "salted out." This is particularly likely to occur if too concentrated solutions are used, or if the test drop is allowed to evaporate to dryness.

7—Some substance not previously known to react under the conditions of the test may be present.

Negative tests are not always to be interpreted as signifying the absence of the substance sought. Lack of positive results may be due to any of a number of reasons, the most common of which are as follows:

1—The substance sought may be absent, or present in quantity below the limit of the reaction employed.

2—Its *effective* concentration may be too low, due to its presence in a complex ion or insoluble or undissociated compound.

3—Precipitation may be inhibited by high acidity or alkalinity, solubility in excess of reagent, or the presence of other interfering substances.

4—The substance may have been decomposed or lost in the process of solution or evaporation, or in other preliminary stages of the analysis.

Substances insoluble in water are likely to be fairly easy to identify after they have been "opened up" or brought into solution, for the very fact of their insolubility limits the possibilities, once some chemical information is available.

Frequently such materials are natural or synthetic minerals, and a knowledge of the methods of identification by "bead" tests, blowpipe reactions, and other methods of the mineralogist affords a great saving of time and labor. The probable associations of elements in minerals will also be a guide to further testing.

The following procedures will be found adequate for dealing with most insoluble materials, but it must be borne in mind that the anion of the substance tested may be affected by them.⁸

1-Treatment with HNO_3 . Use dilute acid and warm gently, replacing evaporation losses. If undissolved, employ concentrated HNO_3 and heat to boiling. The material may be converted to nitrates or oxides.

Evaporate some of the HNO_3 solution to dryness, to note the amount dissolved, and the possible presence of isotropic crystals (Ca, Sr, Ba, Pb nitrates, or As_2O_3).

2-Treatment with aqua regia may be successful if HNO_3 fails as a solvent. The material may be converted to chlorides.

3-Concentrated H_2SO_4 may serve to dissolve insoluble sulphates, and their cations may be recognized on recrystallization from it. (See page 96.) Salts of volatile acids will be converted to sulphates.

4-Alkalis such as NaOH or KOH, in solution, or used for fusions in a tiny cup of silver, nickel, or iron, sometimes serve for "opening up" minerals. Anions are likely to be transposed more or less completely by such treatment.

Na_2CO_3 in concentrated solution may, on long boiling, effect a transposition of ions. All or part of the anions will be present as soluble sodium salts, and the cations as insoluble oxides or carbonates. Na_2CO_3 is also useful for fusions.

5-HF, $(\text{NH}_4)_2\text{HF}$, or NaF and H_2SO_4 are useful in dealing with insoluble oxides or silicates. Reactions with fluorides should be employed only as a last resort, on account of the risk of injury to lenses.

Substances soluble in water, or solutions obtained from the treatment of insoluble materials, may be tested according to various procedures, depending on the completeness of the information desired.

Tests for the presence or absence of a single ion require only that the solution shall be of the optimum concentration to yield a conclusive test, and that interfering substances shall be absent.

⁸ Repeated evaporations with concentrated acids, or long heating with volatile solvents, may result in a concentration of the small amounts of impurities present in these liquids, to a point where they yield positive tests. Blank treatments will eliminate the risk of misinterpretations due to such causes.

In dealing with material of unknown composition, various concentrations of sample and of the reagent should be tried. Care should be taken to avoid the presence of strong acids, if the precipitate sought is the salt of a weak acid.

More than one reagent should be used in most cases, especially if the results are at all doubtful, and it is well to transform the precipitate first obtained successively into several different characteristic compounds of the material found, as confirmation of its identity.

It may happen, as in spectroscopic analysis, that traces or impurities are only detectable after a preliminary chemical separation from the substance which constitute the bulk of the sample. Frequently microscopical tests can be employed in connection with operations on a larger scale, as in the identification of small amounts of precipitates obtained in macroscopic qualitative analysis. The procedures of inorganic and analytical chemistry appropriate to such separations or concentrations will depend on the nature of the sample and of the ions to be tested for, and cannot be discussed here.

Tests for members of a group are often valuable as rapid means of furthering the course of the analysis, or of eliminating a number of possibilities at once. Reagents such as metallic zinc or magnesium, "zinc sulphide fibers," ammonium hydroxide, hexamethylenetetramine, or potassium xanthate, may serve to point the way to subsequent identity tests for individual cations. More specific reagents, such as cesium chloride, potassium mercuric thiocyanate, oxalic acid, hydrochloric acid, or sulphuric acid, may be used similarly, and will frequently serve for specific identifications, confirmatory tests being applied if necessary. Such group tests will ordinarily be applied on separate small portions of the solution, though in some instances it may be feasible to add a second reagent to a drop in which no positive results have been obtained in the first test.

In identifying anions the reagents of the Bunsen-Treadwell system, BaCl_2 and AgNO_3 , are employed in like manner. It may sometimes be useful to test for the anions of volatile acids, by heating with H_2SO_4 or $\text{HC}_2\text{H}_3\text{O}_2$.

Tests for cations, as employed in microscopic qualitative analysis, will not ordinarily be carried out in a fixed sequence or in accordance with a systematic analytical scheme. Instead, the

preliminary tests with the group reagents mentioned above will point fairly positively to a limited number of possibilities, and these should then be sought by means of identity tests. In general, it is well to make a list of all the ions which may be present and to check off from this list all those individuals or groups which have been positively eliminated. Otherwise there is a likelihood that the analyst may neglect to test for certain ions which do not appear in the various groups.

A single solid phase should not be assumed to be a simple salt; it may be a double or mixed salt, or a solid solution. The probable associations of ions in such cases will afford a useful guide to judicious testing; for instance, most double salts contain one of the alkali metals, and solid solutions ordinarily contain ions belonging to the same chemical family or at least having like valence.

Examination of Alloys.—The material, in the form of fine filings or borings, is dissolved in a tiny crucible or watch-glass, by means of the appropriate solvent. A streak on a plate of ground glass may be dissolved by adding a drop of solvent, and decanting. A very minute amount of metal will yield several drops of a relatively concentrated solution.

Non-ferrous alloys are best dissolved in HNO_3 . Sn (and possibly Sb, P, As, W, Si, Ti, and Zr) may remain as an insoluble oxide residue, which may adsorb some of the soluble nitrates. It is essential that all the metal shall have been brought into solution, lest some of the more noble constituents "plate out" upon the undissolved portion.

Separations and tests may be carried out according to the following schemes, but every possible short cut should be utilized.

Scheme for the Qualitative Analysis of Common Non-Ferrous Alloys⁹

Dissolve in concentrated HNO_3 . Evaporate to a syrupy consistency or to a moist mass on water bath. Do not carry to complete dryness. Add water and again evaporate. Extract with *warm* water. Filter.

⁹ Method of Whitmore and Schneider: *Ind. Eng. Chem. (Anal. Ed.)* **2**, 173 (1930). Slightly modified.

Residue A As; Sb; Bi; Sn

(Traces of Pb; Cu etc.)
Remove a little of the residue and test it for As by conversion into H_3As . (See page 199.)

Dissolve the remainder of residue *A* in aqua regia. Divide into three parts.

1-Test with CsCl . Or reduce with metallic Fe to SnCl_2 and test for Sn.

2-If Sn is absent test for Sb with CsCl ; if Sn is present convert into potassium antimonate and test with Na = Sodium pyroantimonate.

3-Test with CsCl and confirm by conversion into sodium or potassium bismuth sulphate.

Filtrate I Add NH_4Cl and NH_4OH Filter = *Filtrate III*. Precipitate *B*.

Precipitate B Fe; Cr; Al; Pb; Hg Dissolve in the least possible volume of dilute HCl . Add NaOH in excess. Add Na_2O_2 , boil, filter = *Filtrate II*. Precipitate *C*.

Precipitate C Hg, Fe

Dissolve in dilute HCl . Divide into two parts.

1-Test for Hg with KI . Or treat with metallic copper, sublime the Hg and convert the globules into HgI_2 with iodine. (See page 146.)

2-Test for Fe with KSCN or $\text{K}_4\text{Fe}(\text{CN})_6$.

Filtrate II Al; Pb; Cr

Acidify with acetic acid.
Divide into three parts.

1-Test for Pb with KI after adding HNO_3 .

2-Test for CrO_4^{--} with AgNO_3 (See page 336). (Silver acetate may be precipitated.)

3-Precipitate all the lead as PbSO_4 . Centrifuge. Concentrate. Test for Al with Cs_2SO_4 . (See page 162.)

Filtrate III Mn; Ni; Co; Zn

Add H_2O_2 , boil and filter = *Filtrate IV*. Precipitate *D*.

Precipitate D Mn; Co; Ni

Divide into three parts.

1-Fuse with Na_2CO_3 ; green color = Mn. Or test for Mn with sodium bismuthate. (See page 235.)

2-Dissolve in HCl and test for Ni with dimethylglyoxime. (See page 246.)

3-Dissolve in HCl and test for Co with $\text{K}_2\text{Hg}(\text{SCN})_4$. (See page 241.) Or test with sodium nitrite. (See page 241.)

Filtrate IV Cu; Zn; Cd; Ni; Mg

Acidify with HCl. Add Na_2SO_3 and NH_4SCN , boil and filter = *Filtrate V*. Precipitate *E*.

Precipitate E Cu

Dissolve in HCl. Test for Cu with $\text{K}_2\text{Hg}(\text{SCN})_4$. (See page 249.)

Filtrate V Zn; Cd; Ni; Mg

Add NH_4OH in slight excess. Divide into three parts.

1—Acidify with HCl . Test for Zn, Cd, with $\text{K}_2\text{Hg}(\text{SCN})_4$. (See page 124.)

2—Test for Ni with dimethylglyoxime.

3—Add HN_3PO_4 . Decant, filter or centrifuge. Dissolve the precipitate in the least amount of HCl . Reprecipitate the Mg as $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ with NH_4OH . Or add $\text{NaC}_2\text{H}_3\text{O}_2$ and $\text{HC}_2\text{H}_3\text{O}_2$ and test with $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$. (See page 121.)

Noble metals, and members of the platinum group, may be analyzed by the methods suggested on pages 274 and 276.¹⁰

Ferrous alloys are best attacked by HCl or H_2SO_4 (dilute). Stainless steels and other acid-resistant alloys may require treatment with aqua regia. The analysis can conveniently be based upon the following scheme.

Scheme for the Qualitative Analysis of Ferrous Alloys¹¹

Dissolve the filings or borings in a very small volume of H_2SO_4 (1 : 3) in a *covered* crucible (Fig. 6). Warm gently until completely dissolved; then add a little more of the sample, cover tightly and allow to stand until *all* the iron is reduced to the ferrous condition. Dilute and filter; wash the residue with acidulated water. Work quickly to prevent oxidation.

Residue A W; Si; C

Together with traces of other elements. Fuse with $\text{K}_2\text{S}_2\text{O}_7$. Extract the fusion with water acidulated with H_2SO_4 . Filter; discard filtrate.

¹⁰ See also the methods of Strebing and Holzer: *Mikrochemie* **8**, 264–70 (1930).

¹¹ Based upon methods of Moore and coworkers: Bul. **212**, Bureau of Mines, Washington, 1923.

Residue B W; Si

Test, (See page 173). Remove Si as SiF_4 . Ignite residue = WO_3 . Test by Methods B, C, pages 221, 222.

Filtrate I, from *Residue A*

Fe; Al; Ti; Zr; Mo; U; V; As; P; Cr

Add NH_4OH , *carefully avoiding an excess*. Filter. If all the Fe was in the ferrous condition and no excess of NH_4OH was added the filtrate will consist of FeSO_4 -(NH_4) $_2\text{SO}_4$ in solution. *Residue C*.

Residue C

Dissolve in the least amount possible of HNO_3 (1 : 1). Add Na_2O_2 until all the HNO_3 is neutralized. Add Na_2CO_3 ; warm gently; *Filtrate II*. *Precipitate D*.

Precipitate D Fe; Ti; Zr (with a small amount of V and P.)

Wash with a solution of NH_4NO_3 . Dissolve in H_2SO_4 (1 : 5). Test for Ti and Zr. (See pages 173, 176.)

Filtrate II Al; Mo; U; V; As; P; Cr (with traces of Ti and Zr)

Evaporate to small volume. Add HNO_3 (1 : 1) until almost neutral. This should precipitate Al as hydrous oxide or phosphate or both, providing that the Al is in considerable excess of the P (about 10 : 1). Add to the turbid solution $(\text{NH}_4)_2\text{CO}_3$. Allow to stand a short time. Filter = *Filtrate III*. *Precipitate E*.

Precipitate E Al; P

Wash. Test one portion for Al by cesium sulphate. Test another portion for P. (See page 197.)

Filtrate III Mo; U; V; As; P; Cr (Ti, Zr)

Acidify with HNO_3 . Boil to remove CO_2 . Add NH_4OH (1 : 1). Acidify with HNO_3 . Add $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Filter = *Filtrate IV*. *Precipitate F*.

Precipitate F Mo; V; As; Cr

Dissolve in HNO_3 . Fume with H_2SO_4 ; dilute; filter or centrifuge to remove PbSO_4 . Test for As by conversion into H_3As , page 199. For Cr by conversion into CrO_4^{--} .

For V by conversion into ammonium metavanadate and recrystallization from acetic acid.

Filtrate IV U

Remove the Pb as PbSO_4 . Precipitate the U with NH_4OH giving ammonium uranate.

Tests for anions should be carried out according to the Bunsen-Treadwell system. (See page 288.) The original solution of the unknown may be used, or that obtained on transposition with Na_2CO_3 , in which only the sodium salts of the various acids are present. It is necessary to bear in mind that treatment with strong acids or oxidizing agents, fusions, interaction with other anions, or even exposure to the air may cause alteration of an anion and invalidate the ultimate tests.

In general it is advisable first to separate the great groups, with AgNO_3 and with BaCl_2 , and to treat the resulting precipitate further with HNO_3 or other acid, and with whatever specific reagents can be properly applied, in order to identify the anions present.

APPENDIX

PREPARATION OF SPECIAL REAGENTS

Preparation of Potassium Mercuric Thiocyanate.—The potassium double salt $K_2Hg(SCN)_4$ is preferable to the corresponding ammonium and sodium salts, which are deliquescent. It is of higher solubility than $KHg(SCN)_3$, and occurs as monoclinic tablets.¹ Either of the following methods of preparation is satisfactory:

1. Dissolve a known amount of KSCN in a small volume of water; add the equivalent quantity of freshly precipitated and washed $Hg(SCN)_2$. (Do not use the material which is marketed in stick form.) Dilute, with stirring, until complete solution is obtained, and evaporate to dryness at room temperature, preferably in a desiccator.

2. Dissolve 3 to 5 parts of KSCN and 1 part of $Hg(SCN)_2$ in a minimum quantity of water, and evaporate in a desiccator. Collect the first crop of tabular crystals, wash with alcohol, and dry.

Preparation of Potassium Ethyldithiocarbonate (Potassium Xanthate).²—To 25 cc. of 95 per cent alcohol add 5 grams of KOH. Warm gently until no more KOH dissolves. Cool and decant the clear, supernatant solution. Add 10 cc. of carbon disulphide. Shake thoroughly in a stoppered flask. Chill in ice water until the potassium ethyldithiocarbonate has completely separated, and while the preparation is still cold add sufficient ether to dissolve the unacted-upon alcohol and carbon disulphide. Filter upon a Witt plate or Buchner funnel. Suck dry and wash the fine crystals thoroughly with ether. Spread out the crystal upon filter paper until the ether has evaporated and transfer to a well-stoppered container.

¹ The physical chemistry of the double thiocyanates of potassium and mercury is discussed by Mason and Forgeng: *Jour. Phys. Chem.* **35**, 1123 (1931).

² Kotten: *Chemist-Analyst*. No. 48. Nov.-Dec. 1926.

Preparation of Cesium Sulphate. — To a small volume of dilute sulphuric acid add cesium chloride in an amount very slightly in excess of that required to convert all the SO_4 to Cs_2SO_4 . Heat gently and when dry slowly raise the temperature until fumes of SO_3 just begin to appear. Cool, dissolve in water, and evaporate to crystallization.

Preparation of Fibers Impregnated with Litmus. — A good quality of raw silk is boiled in water containing a little soap, rinsed thoroughly and placed for two hours at room temperature in a sodium hydroxide solution containing 10 grams sodium hydroxide in 100 cc. of water. The silk is then thoroughly washed with distilled water. Dyeing this treated silk in a 10 per cent solution of purified litmus,³ acidified with 3 or 4 drops of 1 : 4 sulphuric acid, produces a fiber of the proper color intensity. In order to dye the silk properly, the acid litmus solution containing it is evaporated to a thick syrup, the silk then removed and washed in running water, neutralized carefully with very dilute sodium hydroxide solution, and again washed thoroughly. If red and blue varieties of the silk are desired, these neutral-tinted fibers may be treated with dilute acetic acid for red or with dilute sodium hydroxide for blue, and then washed thoroughly in running water.

The sensitiveness of the litmus silk depends upon the degree of adsorption of the dye, the degree of purification of the raw silk, and the degree of purification of the litmus.

If too little dye is adsorbed the color change is not distinct enough. If too much dye is adsorbed the fiber becomes less sensitive, and the color is so deep that it renders the fiber opaque.

The greater the degree of purification of the litmus the more sensitive the dyed fiber, though this factor is not as important as the two former ones.

Preparation of Purified Litmus. — The following procedure (essentially Wartha's method)⁴ is suggested for obtaining an exceedingly pure litmus. Commercial litmus "cubes" are extracted with 95 per cent alcohol until the alcoholic extract no longer has a reddish tinge. They are then repeatedly extracted with water

³ Chamot and Cole: *Jour. Ind. Eng. Chem.* **9**, 969 (1917).

⁴ *Berichte* **9**, 217 (1876).

until the greater part of the coloring matter is removed, a current of air being blown through the solution to prevent reduction. The filtered solution is carried to a thick syrup in an evaporator on the water bath. The mass is then evaporated several times with portions of absolute alcohol acidified with acetic acid in order to destroy carbonates, and the residue is extracted repeatedly with absolute alcohol as long as the alcohol has a reddish color by reflected light. The residue is dissolved in water, concentrated to a thick syrup and treated with absolute alcohol. The pasty mass is stirred with absolute alcohol until the portions poured off no longer contain any red coloring matter. The final residue is dissolved in distilled water, concentrated to a thick syrup and poured into absolute alcohol. The semi-solid gummy precipitate is spread on a plate and dried at 70° to 80° C. The pigment as thus obtained forms a hard tenacious mass, easily soluble in water, and yields an indicator of great sensitiveness, changing at once to red or blue with acid or alkali.

Preparation of Fibers Impregnated with Congo Red. — Of the common textile fibers tested, silk and viscose were found to be the most suitable for the preparation of Congo red fibers, the latter giving an even more sensitive fiber than the former.

The best concentration of the dye for the silk fibers was found to be a 0.5 per cent solution, made alkaline with sodium hydroxide. For the preparation of the Congo red viscose-silk fibers, a somewhat more concentrated solution is advisable. Dyeing in a 2 per cent alkaline solution of Congo red for 15 minutes, washing thoroughly and then drying by pressing between filter papers, was found to yield an eminently satisfactory fiber.

Congo red fibers can be used in the red form only, as the blue form is unstable in the air. For the detection of acidity they compare favorably with the litmus fibers, having the same degree of sensitiveness.

Although Congo red is employed as an indicator in analytical work for the purpose of differentiating between organic and inorganic acids, Congo red fibers are far too sensitive for this purpose.

Preparation of Fibers Impregnated with Turmeric. — Of the various fibers tested, viscose silk gives by far the best color reaction, flax being next best but less satisfactory in comparison.

No preliminary treatment of the viscose silk to render it more adsorptive is necessary.

A 50 per cent alcoholic, alkaline solution of turmeric is prepared by boiling approximately 20 g. of ground turmeric root with 50 cc. of alcohol and adding to the filtered solution an equal volume of water and $\frac{1}{2}$ to 1 cc. of dilute sodium hydroxide (10 per cent). The fibers are immersed in this solution which is then evaporated on a water bath⁵ to a syrupy consistency. The fibers are removed and immediately dipped in 95 per cent alcohol, pressed between filter paper, dipped in a dilute aqueous solution of sulphuric acid, washed with water and dried. The transference of the fibers from the hot dye to the alcohol must be done quickly as otherwise the turmeric adhering to the fibers is removed only with difficulty. Too long an immersion in the alcohol tends to remove the adsorbed dye as well as the excess dye.

If the fiber still appears to have any unadsorbed turmeric adhering to it (with viscose silk this is easily noted by the lack of luster) it can once more be dipped in alcohol and washed with water. Any unadsorbed turmeric interferes with the formation of the blue color in the boron test. This method as given yields a beautiful golden yellow product which was found to be eminently satisfactory.

Preparation of Wool Impregnated with Zinc Sulphide. — The defatted wool is swelled by soaking over night at room temperature, in a 1 per cent solution of sodium hydroxide. It is then washed and dipped 5 or 6 times alternately in solutions of 10 per cent zinc acetate and 10 per cent sodium sulphide, pressing out the excess solution but not washing between dippings. After the final dipping, the impregnated wool is washed and dried by pressing between filter paper. Zinc sulphide wool fibers made in this way are sensitive to 1 μ g. of copper per drop. The sodium sulphide solution should be freshly prepared by passing H_2S into a solution of $NaOH$, until a portion removed fails to yield a precipitate with $MgCl_2$. The fat may be removed from the wool by a mixture of alcohol and ether.

⁵ When preparing or working with fibers impregnated with turmeric all contact with "resistance" glass vessels or object slides is to be avoided, since glass of this variety usually contains boron.

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PERIODIC TABLE OF THE CHEMICAL ELEMENTS—1929

THE FIGURE ABOVE THE NAME OF EACH ELEMENT IS ITS ATOMIC NUMBER AND THAT BELOW, ITS ATOMIC WEIGHT

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
I		1 Hydrogen H 1.008							
II	2 Helium He 4.0	3 Lithium Li 6.94	4 Beryllium Be 9.02	5 Boron B 10.82	6 Carbon C 12.00	7 Nitrogen N 14.008	8 Oxygen O 16.00	9 Fluorine F 19.0	
III	10 Neon Ne 20.2	11 Sodium Na 23.00	12 Magnesium Mg 24.32	13 Aluminum Al 26.9	14 Silicon Si 28.06	15 Phosphorus P 31.04	16 Sulphur S 32.06	17 Chlorine Cl 35.46	
IV	18 Argon A 39.94	19 Potassium K 39.10	20 Calcium Ca 40.07	21 Scandium Sc 45.10	22 Titanium Ti 47.90	23 Vanadium V 50.96	24 Chromium Cr 52.01	25 Manganese Mn 54.93	26 Iron Fe 55.84
		29 Copper Cu 63.57	30 Zinc Zn 65.38	31 Gallium Ga 69.72	32 Germanium Ge 72.60	33 Arsenic As 74.96	34 Selenium Se 79.20	35 Bromine Br 79.92	27 Cobalt Co 58.94
V	36 Krypton Kr 82.90	37 Rubidium Rb 85.44	38 Strontium Sr 87.63	39 Yttrium Yt 88.92	40 Zirconium Zr 91.22	41 Columbium Cb 93.10	42 Molybdenum Mo 96.00	43 Masurium Masurium	44 Ruthenium Ru 101.70
		47 Silver Ag 107.8	48 Cadmium Cd 112.41	49 Indium In 114.80	50 Tin Sn 118.70	51 Antimony Sb 121.77	52 Tellurium Te 127.50	53 Iodine I 126.92	45 Rhodium Rh 102.91
VI	54 Xenon Xe 130.20	55 Cesium Cs 132.81	56 Barium Ba 137.37	57-71 Rare Earths*	72 Hafnium Hf 178.60	73 Tantalum Ta 181.50	74 Tungsten W 184.00	75 Rhenium Re 188.7	46 Palladium Pd 106.70
		79 Gold Au 197.20	80 Mercury Hg 200.61	81 Thallium Tl 204.39	82 Lead Pb 207.22	83 Bismuth Bi 209.00	84 Polonium Po (210)	76 Osmium Os 190.80	77 Iridium Ir 193.10
VII	86 Radon Rn 222.00	87 —	88 Radium Ra 226.95	89 Actinium Ac	90 Thorium Th 232.15	91 Uranium X, (Brevium)	92 Uranium U 238.17	—	78 Platinum Pt 195.23
* Rare Earths									
	57 Lanthanum La 138.90	58 Cerium Ce 140.25	59 Praseodymium Pr 140.92	60 Neodymium Nd 144.27	61 Promethium Pm (209)	62 Samarium Sm 150.43	63 Europium Eu 152.00	64 Gadolinium Gd 157.26	
		65 Terbium Tb 158.90	66 Dysprosium Dy 162.50	67 Holmium Ho 164.93	68 Erbium Er 167.26	69 Thulium Tm 168.93	70 Ytterbium Yb 173.04	71 Lutetium Lu 175.00	

LABORATORY CHEMICAL MICROSCOPY — CORNELL UNIVERSITY

KEY TO REAGENTS IN REAGENTS BLOCKS

	1	2	3	4	5	6	7	8	9	10	11	12
A	Silver Nitrate	Thallous Nitrate	Potassium Thiocyanate	Calcium Acetate	Potassium Sulphate	Sodium Sulphate	Sodium Bicarbonate	Potassium Chlorate	Potassium Bichromate	Oxalic Acid	Litmus Silk	Ammonium Fluoride
B	Chloroplatinic Acid	Perchloric Acid	Dimethyl Glyoxime	Cobalt Acetate	Mercurous Nitrate	Mercuric Chloride	Ammonium Carbonate	Ammonium Persulphate	Potassium Chromate	Potassium Oxalate (Acid)	Antimony Chloride	Cesium Sulphate
C	Barium Chloride	Hydroxylamine HCl	Strontium Acetate	Copper Acetate	Potassium Nitrite	Lead Acetate	Sodium Carbonate	Ammonium Chloride	Potassium Ferrocyanide	Ferric Chloride	Hexamethylene tetramine	Nitron Sulphate
D	Cesium Chloride	Phenylendiamine HCl	Sodium Bismuthate	Zinc Acetate	Sodium Thio-sulphate	Arsenic Acid	Potassium Xanthate	Citric Acid	Potassium Permanganate	Magnesium Chloride	Turneric Viscose-silk	Copper
E	Potassium Mercuric Thiocyanate	Potassium Iodide	Sodium Hydroxide	Sodium Acetate	Ammonium Acetate	Uranyl Acetate	Bismuth Sulphate	Di-sodium Phosphate	Ammonium Molybdate	Starch	Zinc Sulphide Wool	Zinc
	1	2	3	4	5	6	7	8	9	10	11	12
Arsenic Acid.....6D												
Ammonium.....5E												
Carbonate.....7B												
Chloride.....8C												
Fluoride.....12A												
Molybdate.....9E												
Persulphate.....8B												
Antimony Chloride.....11B												
Barium Chloride.....1C												
Bismuth Sulphate.....7E												
Calcium Acetate.....4A												
Cesium Chloride.....1D												
Cesium Sulphate.....12B												
Chloroplatinic Acid.....1B												
Citric Acid.....8D												
Cobalt Acetate.....4B												
Copper Metal.....12D												
Copper Acetate.....4C												
Dimethyl Glyoxime.....3B												
Ferric Chloride.....10C												
Hexamethylenetetramine.....11C												
Hydroxylamine HCl.....2C												
Lead Acetate.....6C												
Litmus Silk.....11A												
Magnesium Chloride.....10D												
Mercuric Chloride.....6B												
Mercurous Nitrate.....5B												
Nitron Sulphate.....12C												
Oxalic Acid.....10A												
Perchloric Acid.....2B												
m-Phenylenediamine HCl.....2D												
Potassium Bichromate.....9A												
Chromate.....8A												
Ferrocyanide.....9C												
Iodide.....2E												
Mer. Thiocyanate.....1E												
Nitrite.....5C												
Oxalate.....10B												
Permanganate.....9D												
Sulphate.....5A												
Thiocyanate.....3A												
Xanthate.....7D												
Silver Nitrate.....1A												
Sodium Acetate.....4E												
Sodium Bicarbonate.....7A												
Bismuthate.....3D												
Carbonate.....7C												
Hydroxide.....3E												
Phosphate.....8E												
Sulphate.....6A												
Thiosulphate.....5D												
Starch.....10E												
Strontium Acetate.....3C												
Thallous Nitrate.....2A												
Turneric Viscose-silk.....11D												
Uranyl Acetate.....6E												
Zinc Acetate.....4D												
Metal.....12E												
Sulphide Wool.....11E												

CAUTION. — Never remove from the block more than one vial at a time.

Use special care to avoid mixing stoppers and contaminating reagents.

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